

## Supporting materials

### **Assignment of protonated *R*-homocitrate in extracted FeMo-cofactor of nitrogenase *via* vibrational circular dichroism spectroscopy**

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**Supplementary Fig. 1.** Syntheses and possible transformations of dinuclear oxidomolybdenum(V) triazole lactates 1, 2 and glycolates 3 respectively.

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**Supplementary Fig. 4.** 2D layered diagrams in  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1).

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**Supplementary Fig. 13.** Optimized molecular structure of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1). Color: molybdenum, violet; oxygen, red; nitrogen, blue; carbon, gray; sulfur, yellow; hydrogen, white.

**Supplementary Fig. 14.** Optimized molecular structure of  $\Delta\text{-Mo}^*\text{Fe}_7\text{S}_9\text{C}[\text{R}(\text{H})\text{homocit}^*](\text{NMF})_2$  (20). Color: molybdenum, violet; oxygen, red; nitrogen, blue; carbon, gray; sulfur, yellow; hydrogen, white; iron, slate.

**Supplementary Fig. 15.** IR spectra of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1),  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2), and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{HgIyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3), in the region of 4000 ~ 450  $\text{cm}^{-1}$ .

**Supplementary Fig. 16.** IR spectra of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1),  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{HgIyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3), in the region of 600 ~ 460  $\text{cm}^{-1}$ .

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**Supplementary Fig. 20a.** TG-DTG curves of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1).

**Supplementary Fig. 20b.** TG-DTG curves of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).

**Supplementary Fig. 20c.** TG-DTG curves of  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{HgIyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

**Supplementary Fig. 21.** TG-DTA curves of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1, a),  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2, b) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{HgIyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3, c).

**Supplementary Fig. 22.** X-bands of EPR spectra for  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})] \cdot \frac{1}{2}\text{H}_2\text{O}$  (1),

$[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2) and  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3) in solid states at 90 K.

**Supplementary Table 1.** Crystallographic data and structural refinements for complexes  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2), and  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

**Supplementary Table 2.** Selected hydrogen bond distances (Å) and angles (°) in  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1).

**Supplementary Table 3.** Selected hydrogen bond distances (Å) and angles (°) in  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).

**Supplementary Table 4.** Selected hydrogen bond distances (Å) and angles (°) in  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

**Supplementary Table 5.** Selected bond distances (Å) and angles (°) for  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1).

**Supplementary Table 6.** Selected bond distances (Å) and angles (°) for  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).

**Supplementary Table 7.** Selected bond distances (Å) and angles (°) for  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

**Supplementary Table 8.** Detail calibrated adsorption data of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> for  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).

**Supplementary Table 9.** Detail calibrated adsorption data of O<sub>2</sub> and N<sub>2</sub> for  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1).

**Supplementary Table 10.** Comparisons of selected bond distances (Å) for  
 $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),

$[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2),

$[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3), (PyH)<sub>2</sub>[Mo<sub>2</sub>O<sub>4</sub>(glyc)<sub>2</sub>Py<sub>2</sub>] (4),<sup>1</sup>

(PyH)<sub>4</sub>[Mo<sub>4</sub>O<sub>8</sub>Cl<sub>4</sub>(glyc)<sub>2</sub>]·2EtOH (5),<sup>1</sup> [Mo<sub>4</sub>O<sub>8</sub>(glyc)<sub>2</sub>Py<sub>4</sub>] (6),<sup>1</sup>

K<sub>6</sub>[(MoO<sub>2</sub>)<sub>8</sub>(glyc)<sub>6</sub>(Hglyc)<sub>2</sub>]·10H<sub>2</sub>O (7),<sup>2</sup> *trans*-[(MoO)<sub>2</sub>O(glyc)<sub>2</sub>(bpy)<sub>2</sub>]·3H<sub>2</sub>O (8),<sup>3</sup>

*trans*-[(MoO)<sub>2</sub>O(R,S-lact)<sub>2</sub>(bpy)<sub>2</sub>]·3H<sub>2</sub>O (9),<sup>3</sup>

*trans*-[(MoO)<sub>2</sub>O(R,S-lact)<sub>2</sub>(phen)<sub>2</sub>]·4H<sub>2</sub>O (10),<sup>3</sup>

Na<sub>2</sub>[Mo<sub>3</sub>(μ<sub>3</sub>-S)(μ<sub>2</sub>-O)<sub>3</sub>(glyc)<sub>3</sub>(2-mim)<sub>3</sub>]·1.5H<sub>2</sub>O (11),<sup>4</sup>

(4-Hmim)<sub>6</sub>[Mo<sub>3</sub>(μ<sub>3</sub>-S)(μ<sub>2</sub>-O)<sub>3</sub>(glyc)<sub>3</sub>(4-mim)<sub>3</sub>]<sub>2</sub>[MoO<sub>2</sub>(glyc)<sub>2</sub>] (12),<sup>4</sup>

Na<sub>3</sub>(4-Hmim)[Mo<sub>3</sub>(μ<sub>3</sub>-S)(μ<sub>2</sub>-O)<sub>3</sub>(SO<sub>3</sub>)(glyc)<sub>3</sub>(4-mim)]·8H<sub>2</sub>O (13),<sup>4</sup>

[Mo<sub>3</sub>SO<sub>3</sub>(glyc)<sub>2</sub>(im)<sub>5</sub>]·im·H<sub>2</sub>O (14),<sup>5</sup> Na<sub>2</sub>[Mo<sub>3</sub>SO<sub>3</sub>(R,S-lact)<sub>3</sub>(im)<sub>3</sub>]·10H<sub>2</sub>O (15),<sup>5</sup>

[Mo<sub>3</sub>S<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>(Hlact)<sub>2</sub>(lact)] (16),<sup>6</sup> K<sub>2</sub>[MoO<sub>2</sub>(glyc)<sub>2</sub>]·H<sub>2</sub>O (17),<sup>2</sup>

[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][MoO<sub>2</sub>(glyc)(Hglyc)] (18),<sup>1</sup> [Na<sub>2</sub>[MoO<sub>2</sub>(S-lact)<sub>2</sub>]]<sub>3</sub>·13H<sub>2</sub>O (19).<sup>2</sup>

**Supplementary Table 11.** The bond distances (Å) of Mo–O<sub>α</sub>-alkoxy/hydroxy, Mo–O<sub>α</sub>-carboxy and C–O<sub>α</sub>-alkoxy/hydroxy in FeMo-cos of nitrogenases (20).

**Supplementary Table 12.** Qualitative assignments of the most intensive bands in VCD spectra of FeMo-co 20 and K<sub>5</sub>[Λ,Λ,Λ,Λ-Mo<sup>\*</sup><sub>4</sub>O<sub>11</sub>(R-Hhomocit<sup>\*</sup>)<sub>2</sub>]Cl·5H<sub>2</sub>O 21.

**Supplementary Table 13.** Comparison of obtained experimental IR, VCD characteristic signals of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{R-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1) in the solid state and assignments of calculated VCD signals from optimized structure of 1.

**Supplementary Table 14.** Comparisons of obtained experimental IR, VCD characteristic signals of extracted FeMo-co  $\Delta$ -Mo<sup>\*</sup>Fe<sub>7</sub>S<sub>9</sub>C[*R*-(H)homocit<sup>\*</sup>](NMF)<sub>2</sub> (**20**) and assignments of calculated VCD signals from optimized structure of **20**.

**Supplementary Table 15.** Bond valence calculations for complexes  
 $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  
 $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2), and  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

**Part II IR spectra of 1,2,4-triazole, lactic acid, *N*-methylformamide, sodium homocitrate,  $\text{K}_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{R,S-H}_2\text{homocit})_2]\cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2[\text{Mo}_3\text{SO}_3(\text{R,S-lact})_3(\text{im})_3]\cdot 10\text{H}_2\text{O}$**

**Supplementary Fig. 23.** FT-IR spectrum of 1,2,4-triazole originated from Spectral Database for Organic Compounds SDBS. URL for this compound: <https://sdb.db.aist.go.jp/sdb/cgi-bin/landingpage?sdbno=3852>.

**Supplementary Fig. 24.** FT-IR spectrum of lactic acid originated from Spectral Database for Organic Compounds SDBS. The  $1047\text{ cm}^{-1}$  peak is assigned to C–OH vibration. URL for this compound: [http://sdb.db.aist.go.jp/sdb/cgi-bin/direct\\_frame\\_disp.cgi?sdbno=12682](http://sdb.db.aist.go.jp/sdb/cgi-bin/direct_frame_disp.cgi?sdbno=12682).

**Supplementary Fig. 25.** FT-IR spectrum of *N*-methylformamide [ $\text{C}_2\text{H}_5\text{NO}$ ] originated from Spectral Database for Organic Compounds SDBS. URL for this compound: [https://sdb.db.aist.go.jp/sdb/cgi-bin/direct\\_frame\\_top.cgi](https://sdb.db.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi).

**Supplementary Fig. 26.** FT-IR spectrum of  $\text{Na}_3(\text{Hhomocit})\cdot\text{H}_2\text{O}$ <sup>7</sup>. The  $1086\text{ cm}^{-1}$  peak is assigned to C–O<sub>H</sub> vibration.

**Supplementary Fig. 27.** FT-IR spectrum of  $\text{K}_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{R,S-H}_2\text{homocit})_2]\cdot 2\text{H}_2\text{O}$ <sup>7</sup>. The peak at  $1084\text{ cm}^{-1}$  is assigned to C–O vibration.

**Supplementary Fig. 28.** FT-IR spectrum of  $\text{Na}_2[\text{Mo}_3\text{SO}_3(\text{R,S-lact})_3(\text{im})_3]\cdot 10\text{H}_2\text{O}$ <sup>5</sup>. The peaks at  $1049$ ,  $1060$  and  $1056\text{ cm}^{-1}$  are assigned to C–O vibration.

## Supplementary Methods

### Part I Syntheses, spectral characterizations and structural analyses for molybdenum $\alpha$ -hydroxycarboxylates

**Physical measurements supplement.**  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , *R*-lactic acid, *S*-lactic acid, glycolic acid, 1,2,4-triazole and  $\text{Na}_2\text{S}_2\text{O}_4$  were purchased from Sigma. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 380 FT-IR spectrometer. Solid state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz Avance III SS-NMR using ADA {Tricyclo[3.3.1.1(3,7)]decane} as an external reference. Solid diffused reflectance UV-Vis spectra were recorded in solid state on a Cary 5000 spectrophotometer in the range of 200 – 800 nm at 293 K. Solid electron paramagnetic resonance (EPR) spectra were analysed by a Bruker EMX-10/12 spectrometer using crystalline samples at 298 K. TG analyses were performed on a Netzsch TG209F1 instrument in  $\text{N}_2$  at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The TG-DTA measurements were conducted on a Netzsch STA 449F5 thermal analysis system in  $\text{N}_2$  atmosphere with a heating rate  $10\text{ }^\circ\text{C min}^{-1}$  over the 30 ~ 1000  $^\circ\text{C}$  range.

**Preparations of  $[\Lambda/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).** Synthesis of **2** was the same as that of **1**, except *S*-lactic acid (1.00 mL, 13.0 mmol) was used instead of *R*-lactic acid. Product **2** was isolated as yellow plates after one week in 43.9% yields (0.722 g) based on molybdenum. Elemental analysis (calc. for  $\text{C}_{12}\text{H}_{19}\text{Mo}_2\text{N}_9\text{O}_9\text{S}$ ): C, 21.9; H, 2.9; N, 19.2%. Found: C, 21.8; H, 2.8; N, 19.2%. mp: 452  $^\circ\text{C}$  (decompose, molybdenum oxide). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3448<sub>br, s</sub>;  $\nu(\text{C-H})$

3127<sub>s</sub>, 2941<sub>m</sub>, 2856<sub>w</sub>;  $\nu_{\text{as}}(\text{CO}_2)$  1638<sub>s</sub>;  $\nu_{\text{s}}(\text{CO}_2)$  1381<sub>s</sub>;  $\nu(\text{Mo}=\text{O})$  977<sub>s</sub>. UV(H<sub>2</sub>O, nm):

322. Solid-state <sup>1</sup>H NMR (400 MHz, ADA, ppm):  $\delta$  8.56 (s, 1H), 3.95 (s, 1H), 0.52 (s, 1H). Solid-state <sup>13</sup>C NMR (400 MHz, 25 °C, ADA, ppm):  $\delta$  = 179.81 (CO<sub>2</sub>), 154.50 – 141.69 (trz), 70.17 (COH), 19.50 (CH<sub>3</sub>).

**Preparation of [Mo<sub>2</sub>O<sub>2</sub>( $\mu$ <sub>2</sub>-S)( $\mu$ <sub>2</sub>-O)(Hglyc)<sub>2</sub>(trz)<sub>2</sub>(H<sub>2</sub>O)] (3).** (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> 4H<sub>2</sub>O (0.883 g, 0.72 mmol) and excess glycolic acid (1.14 g, 15.0 mmol) were dissolved in 5.0 mL water. The pH value of the solution was adjusted to 5.0 with the addition of NaOH. The mixture was heated at 60 °C for 24 hours and cooled to room temperature. Then Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (0.871 g, 5.0 mmol) and 1,2,4-triazole (0.691 g, 10.0 mmol) were added in solution. The pH was justed to 3.0 with concentrated hydrochloric acid. The reactants were heated at 80 °C for 24 hours and cooled to room temperature. Product **3** was isolated as yellow plates in 66.2% yields (0.957 g) based on molybdenum. Elemental analysis (calc. for C<sub>8</sub>H<sub>14</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>10</sub>S): C, 16.6; H, 2.4; N, 14.5%. Found: C, 16.5; H, 2.4; N, 14.6%. mp: 467 °C (decompose, molybdenum oxide). IR (KBr, cm<sup>-1</sup>):  $\nu(\text{OH})$  3460<sub>s</sub>;  $\nu(\text{C}-\text{H})$  3141<sub>s</sub>, 2951<sub>m</sub>, 2563<sub>w</sub>;  $\nu_{\text{as}}(\text{CO}_2)$  1655<sub>vs</sub>;  $\nu_{\text{s}}(\text{CO}_2)$  1359<sub>s</sub>;  $\nu(\text{Mo}=\text{O})$  967<sub>s</sub>. UV(H<sub>2</sub>O, nm): 250. Solid-state <sup>1</sup>H NMR (400 MHz, ADA, ppm):  $\delta$  8.41 (s, 1H), 4.92 (s, 2H). Solid-state <sup>13</sup>C NMR (400 MHz, 25 °C, ADA, ppm):  $\delta$  = 177.87 (CO<sub>2</sub>), 151.65 – 142.26 (trz), 62.86 (COH).

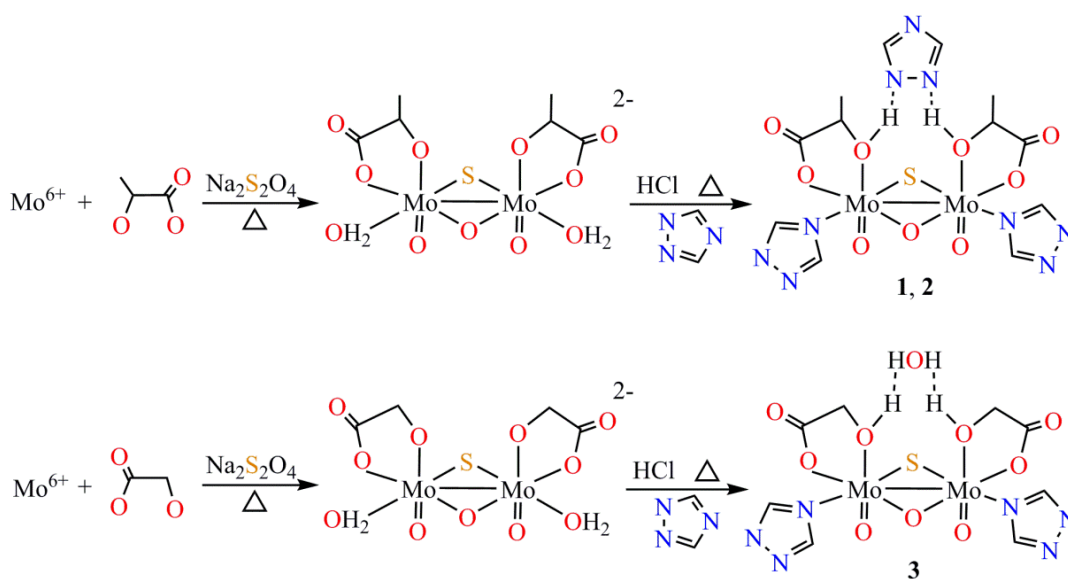
**Preparation of {Na<sub>2</sub>[ $\Delta$ -Mo\*O<sub>2</sub>(*R*-lact\*)<sub>2</sub>]}<sub>3</sub>·13H<sub>2</sub>O.<sup>2</sup>** Sodium molybdate dihydrate (1.21 g, 5.0 mmol) and *R*-lactic acid (1.00 ml, 13.0 mmol) were dissolved in 5.0 ml water. pH value was adjusted to 4.0 with dilute NaOH. The solution was heated at 60 °C for 5 h. The compound was separated as colorless crystals after three days and they

were collected and washed with ethanol. yield: 67.9%. Similarly,  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  was obtained.<sup>2</sup>

**Preparation of  $\text{K}_5[\Lambda, \Lambda, \Lambda, \Lambda\text{-Mo}^*_4\text{O}_{11}(\text{R-Hhomocit}^*)_2]\text{Cl} \cdot 5\text{H}_2\text{O}$  (21).**<sup>8</sup> *R*-homocitric  $\gamma$ -lactone acid (14.0 mg, 0.07 mmol), prepared by the reported method<sup>9</sup> was dissolved in a minimal amount of water. The pH was adjusted by KOH to 11 to generate the acyclic homocitrate as monitored with HPLC. After hydrolysis, potassium molybdate (95 mg, 0.40 mmol) was added in small portions over 10 minutes. Upon cooling in an ice bath for 15 min, the pH of the solution was adjusted to 2.0 with hydrochloric acid to induce complex formation. The salts of chloride were filtrated with precipitation. Complex **21** was formed after sitting at room temperature for four days. Yield: 0.30 mg.

**Gas Adsorption Measurements.** The gas adsorption capacities of **1** ~ **2** were evaluated with a magnetic suspension gravimetric sorption analyzer (ISOSORP-HTGRA) at 298 K at different pressures. Gases adsorption isotherms for pressures up to 30 bar at 298 K was obtained on a magnetic suspension balance (MSB) (RUBOTHERM ISOSORP-HTGRA) operated by MessPro software. In a typical experiment, like the sample **2**, about 112.4 mg, was placed in the sample bucket and loaded in the absorption chamber. The sample was then evacuated at 423 K to remove any traces of water, solvents or dissolved gases until the weight remains constant. The chamber was then pressurized with dry  $\text{O}_2$  at 298 K and the change in weight was monitored by MSB. Each step with different pressure took around 40 min until the adsorption stabilized.

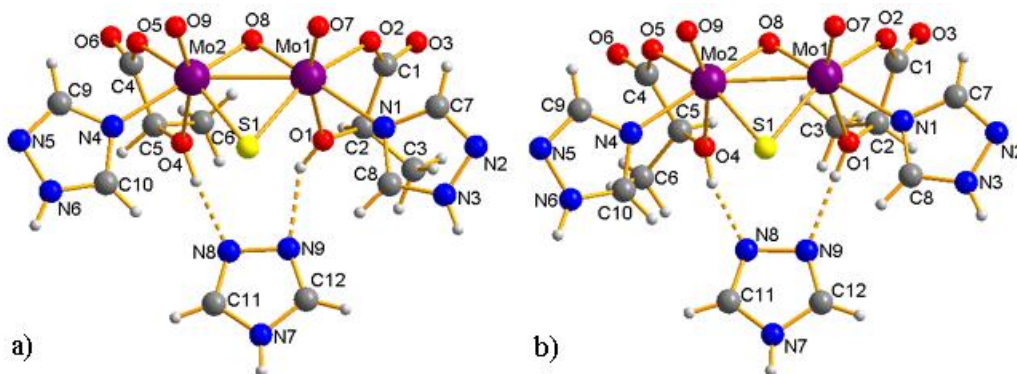
**X-Ray Crystallography.** The crystal data for **1** ~ **3** were collected on an Oxford Gemini CCD diffractometer, with graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 173 K. Multi-scan absorption corrections were applied. The structures were solved by ShelXT and refined by full-matrix least-squares on F<sub>2</sub> using the OLEX<sub>2</sub> crystallographic software package.<sup>10-12</sup> All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were generated geometrically or located from differential Fourier maps and refined isotropically. Crystallographic data and structural refinements for complexes **1** ~ **3** are listed in Supplementary Table 1. CCDC deposition numbers are 1993896 – 1993898.



**Supplementary Fig. 1.** Syntheses and possible transformations of dinuclear oxidomolybdenum(V) triazole lactates **1**, **2** and glycolates **3** respectively.

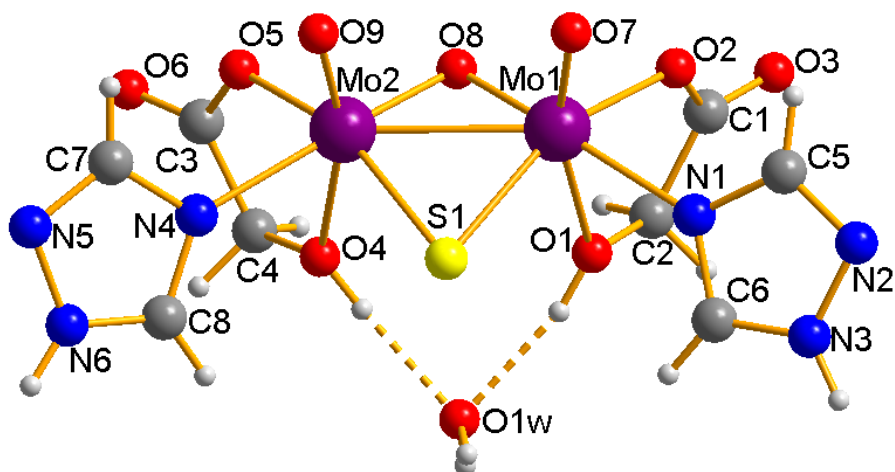
**Syntheses.** Preparations of **1** ~ **3** mainly depend on the requisite proportions of molybdate and ligands, counteranions, pH and the reaction temperature. Compared with the deprotonated molybdenum  $\alpha$ -hydroxypolycarboxylates reported,<sup>2,8,13-22</sup> protonated molybdenum lactates and glycolates in **1** ~ **3** may be attributed to the strong acidity of the solution and multiple *N*-coordination sites with 1,2,4-triazole to stabilize the structures. The favorable pH value was in the range of 2.0 ~ 3.0, increase of pH will lead to failure of the reactions.

Possible syntheses and transformations of oxidomolybdenum(V) triazole lactates and glycolates **1** ~ **3** are outlined in Supplementary Fig. 1. Firstly, dinuclear molybdenum(V) lactate or glycolate  $[\text{Mo}_2\text{O}_2(\mu_2\text{-O})(\mu_2\text{-S})\text{L}_2(\text{H}_2\text{O})_2]^{2-}$  ( $\text{L}$  = lactate/glycolate) formed in reduced solutions with  $\text{Na}_2\text{S}_2\text{O}_4$ , which are similar to molybdenum oxalate  $[\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$  reported.<sup>23</sup> Further substitutions of coordinated water molecules with 1,2,4-triazoles and acidification of lactate or glycolate result in the formations of the final neutral products **1** ~ **3** respectively.



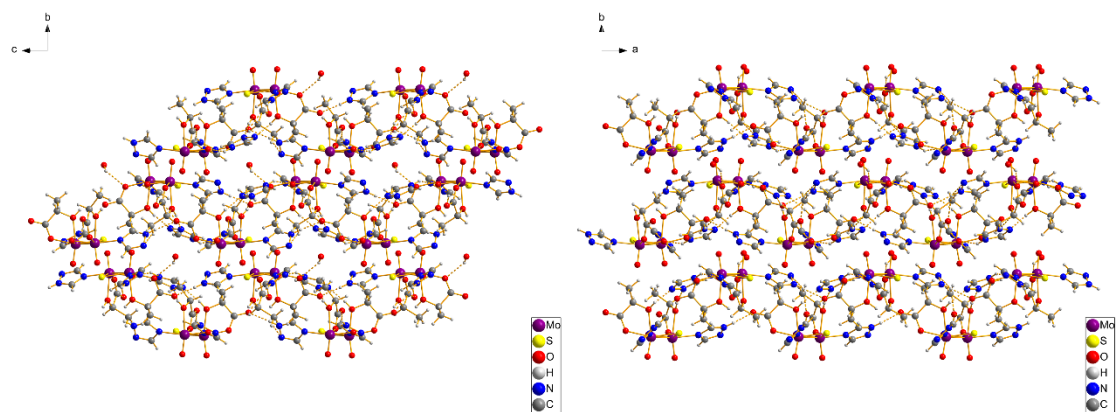
**Supplementary Fig. 2.** Molecular structures of  $[\Delta/\Lambda\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**, a) and its enantiomer  $[\Lambda/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**, b), free water molecule in **1** was omitted for clarity.

**Structural analyses of 1 ~ 2.** As shown in Supplementary Fig. 2, X-ray crystal structures of  $[\Delta/\Lambda\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**) and  $[\Lambda/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**) show a pair of enantiomers with dinuclear molybdenum(V) 1,2,4-triazole lactates. The main structure is the same except for chiral configurations of molybdenum(V) lactates and the number of free water molecules. For **1**, its central core consists of two hexa-coordinated molybdenum atoms in *quasi*-octahedral geometries. The molybdenum(V) atoms are bridged by sulfur and oxygen, and the other corners were completed by *R*-lactates and 1,2,4-triazoles. The lactates in **1** and **2** chelate to molybdenum atoms with  $\alpha$ -hydroxy and  $\alpha$ -carboxy groups respectively. Triazole coordinates to molybdenum atom with nitrogen as monodentate ligand. Free triazole acts as a bridge to connect the dinuclear unit through strong hydrogen bonds with hydroxy groups of lactates [ $\text{O}(1)_{\alpha\text{-hydroxy}} \cdots \text{N}(9)$  2.617(1) Å,  $\text{O}(4)_{\alpha\text{-hydroxy}} \cdots \text{N}(8)$  2.718(1) Å in **1**,  $\text{O}(1)_{\alpha\text{-hydroxy}} \cdots \text{N}(9)$  2.717(8) Å,  $\text{O}(4)_{\alpha\text{-hydroxy}} \cdots \text{N}(8)$  2.609(7) Å in **2**]. This is important to stabilize the protonated structures in **1** and **2**.

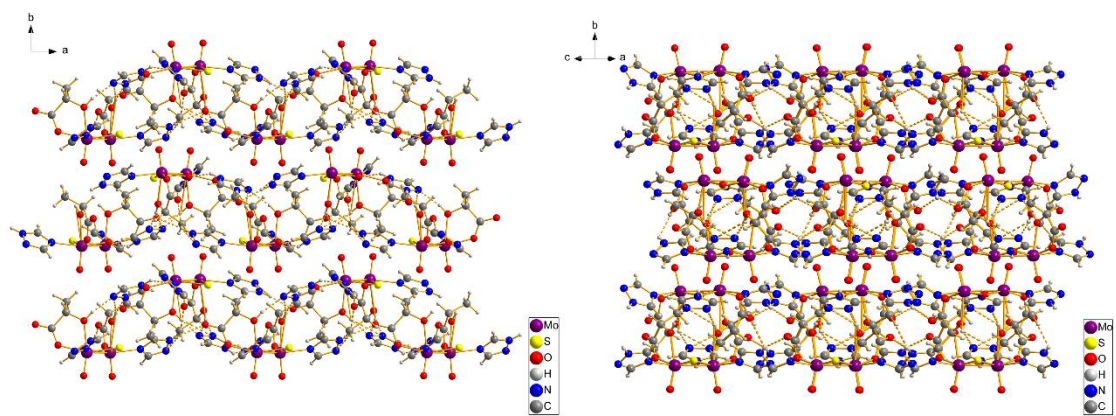


**Supplementary Fig. 3.** Molecular structure of  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**).

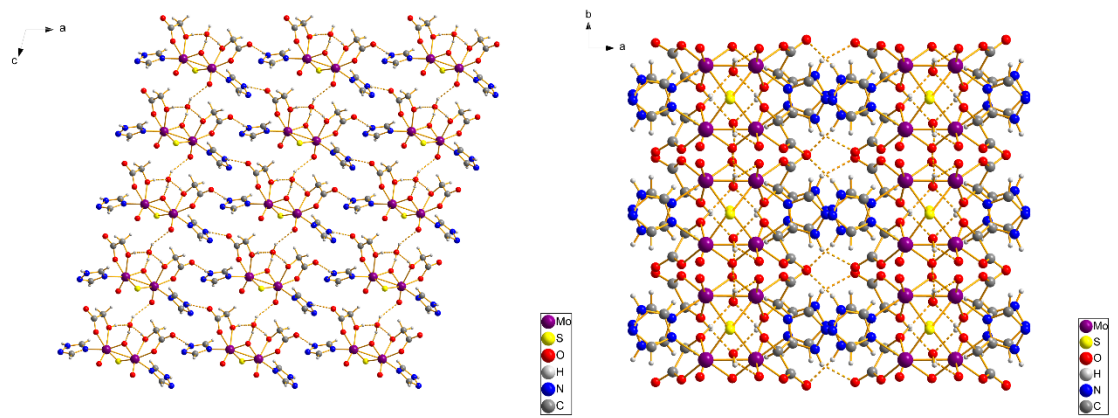
**Structural analysis of 3.**  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**) is a dinuclear mixed ligand molybdenum(V) glycolate as shown in Supplementary Fig. 3. Its main structure is similar to **1**. In **3**, each molybdenum atom is surrounded octahedrally by one  $\mu_2\text{-S}$  and one  $\mu_2\text{-O}$ , one N atom of triazole, two O atoms ( $\alpha$ -hydroxy and  $\alpha$ -carboxy) of glycolate. Free water molecule becomes bridge in the molecule via strong hydrogen bonds  $[\text{O}(1)_{\alpha\text{-hydroxy}} \cdots \text{O}(1\text{w})$  2.675(9) Å,  $\text{O}(4)_{\alpha\text{-hydroxy}} \cdots \text{O}(1\text{w})$  2.675(9) Å]. Unlike **1** or **2**, the protonated structure is stabilized by free water molecule O1w instead of 1,2,4-triazole. The other intermolecular hydrogen bonds are listed in Supplementary Table 4 like  $\text{O}(1\text{w}) \cdots \text{O}(8)_a$  2.670(9) Å  $a(x, 2 - y, \frac{1}{2} + z)$ ;  $\text{O}(1\text{w}) \cdots \text{O}(7)$  3.051(9) Å.

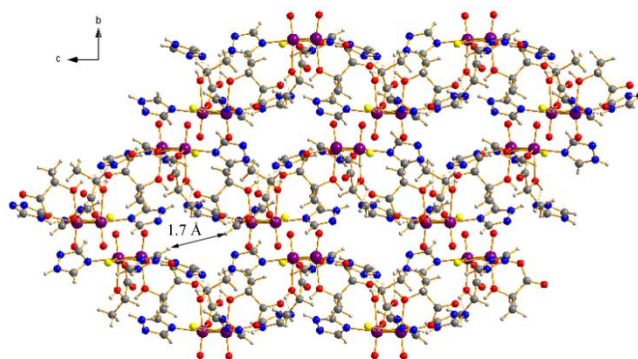


**Supplementary Fig. 4.** 2D layered diagrams in  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**).



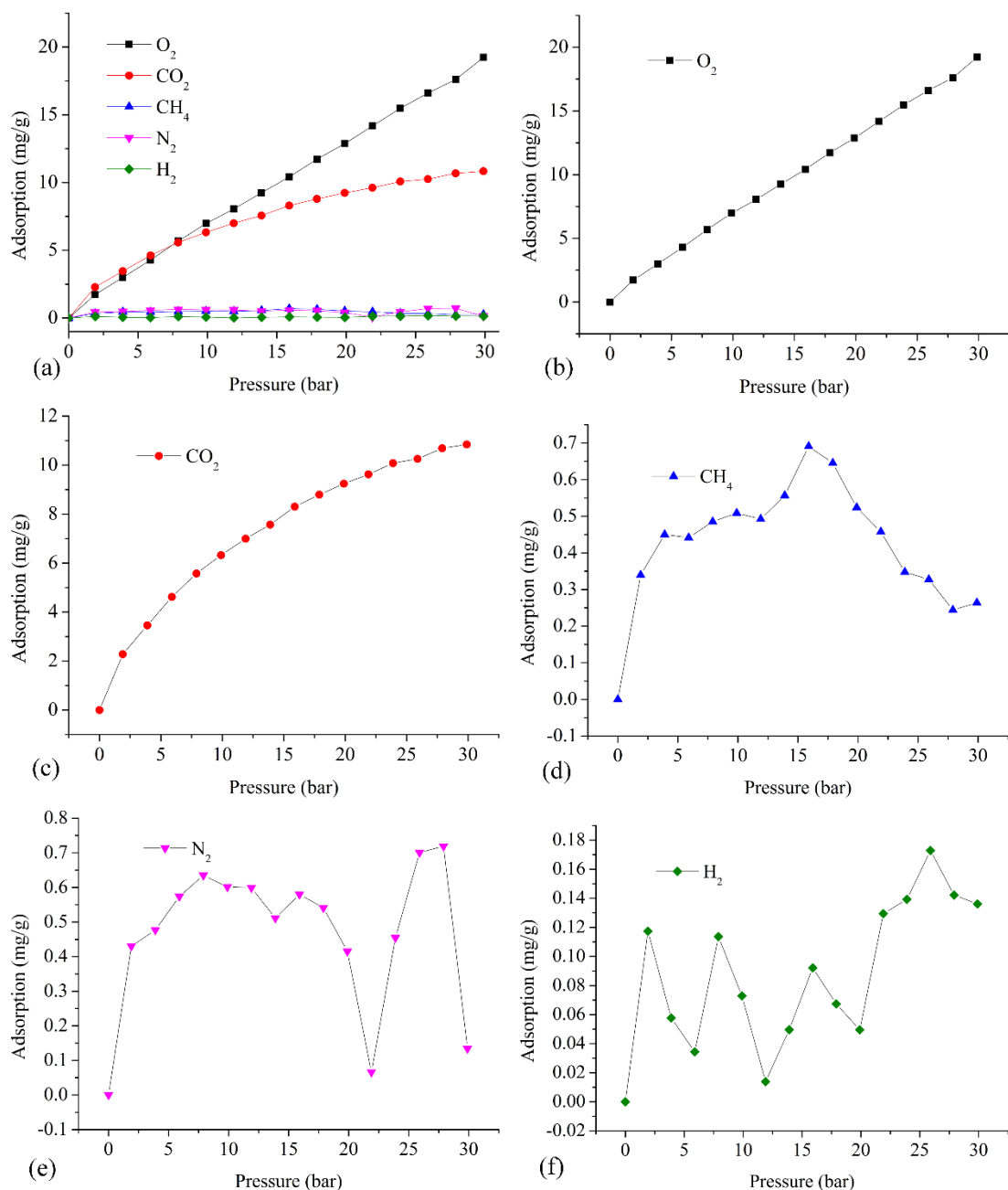
**Supplementary Fig. 5.** 2D layered diagrams in  
 $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2).





**Supplementary Fig. 7.** The channels existed in  $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**) viewed along *a* axis.

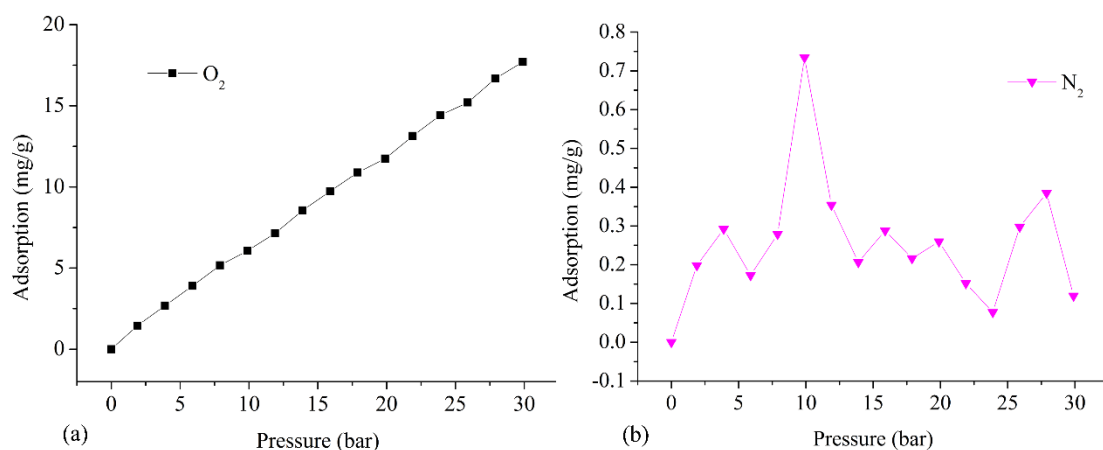
**Channels description in 2.** The minimum inner diameter of the channels existed in **2** is 1.7 Å. The holes exhibit regular oval shape with varying lengths (approximately 5.5 Å long and 2.6 Å wide). The channels are formed by the accumulation of skeletons, and are created by multiple hydrogen bonds between 1,2,4-triazoles and lactates. The smallest constituent unit of the channel includes 12  $\text{Mo}^{5+}$ .



**Supplementary Fig. 8.** (a) Adsorption isotherms of **2** for the gases of O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> at 298 K at different pressures. Independent O<sub>2</sub> (b), CO<sub>2</sub> (c), CH<sub>4</sub> (d), N<sub>2</sub> (e) and H<sub>2</sub> (f) adsorption isotherms of [ $\Lambda/\Delta$ -Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(S-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)] (**2**) at 298 K in different pressures.

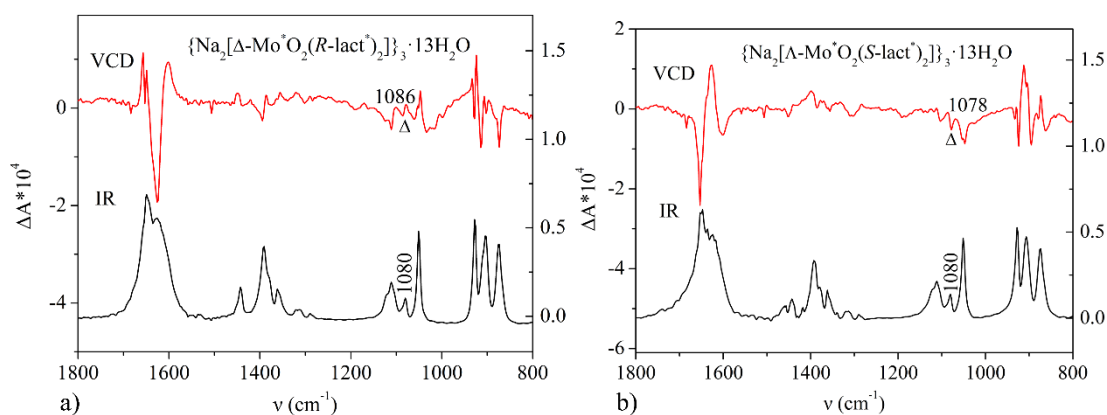
**Adsorption behavior of 2.** There is a small channel (diameter 1.7 Å) existed in the 3D structure of **2** viewed along *a* axis as shown in Supplementary Fig. 7. **2** have been synthesized largely to use for the gas adsorptions of O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub> at 298 K respectively. The results show that the biogases O<sub>2</sub> and CO<sub>2</sub> can be selectively

adsorbed which can be seen in Supplementary Fig. 8a. As the pressure increases, the amount of O<sub>2</sub> adsorbed increases rapidly with 1.72, 5.68, 10.42 and 19.23 mg/g at 1.9, 7.9, 15.9 and 29.9 bar respectively, which have a tendency to attract more as the pressure increases which are shown in Supplementary Fig. 8b. As for CO<sub>2</sub>, the plot in Supplementary Fig. 8c shows an andante increase of CO<sub>2</sub> adsorption as the pressure increases, almost reaching a maximum adsorption value of 10.84 mg/g at 29.9 bar, which is the well-known Langmuir adsorption isotherm (Type I).<sup>24</sup> The other three gases have only little or even no adsorption, which can be seen in Supplementary Figs. 8d ~ 8f. It is noted that the higher selectivities could be obtained at higher pressures, thus **2** could be a promising sorbent for high-pressure air separation.<sup>25</sup> Detail calibrated adsorption data were given in Supplementary Table 8.



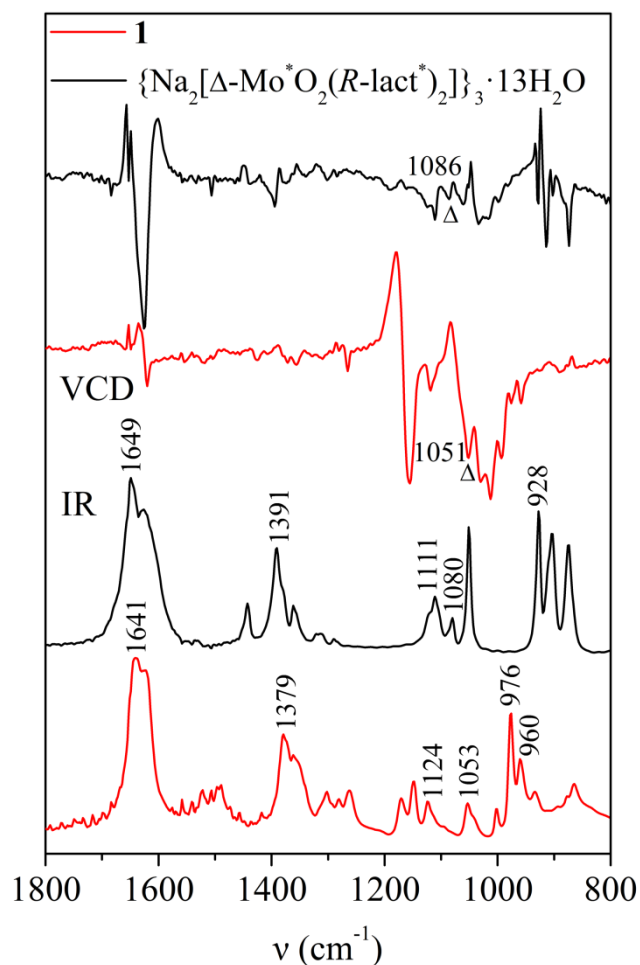
**Supplementary Fig. 9.** Independent O<sub>2</sub> (a) and N<sub>2</sub> (b) adsorption isotherms of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**) at 298 K in different pressures.

**Adsorption behavior of 1.** Similarly, there is an analogous channel existed in the 3D structure of **1** viewed along *a* axis as shown in Supplementary Fig. 4, while a free water molecule existed in the center of the channel through hydrogen bonds. By comparing the O<sub>2</sub> and N<sub>2</sub> adsorption behavior in **1**, **2** in Supplementary Figs. 8 ~ 9, we can find the water molecules in the pores will affect the adsorption performance. Detail calibrated adsorption data for **1** were given in Supplementary Table 9.



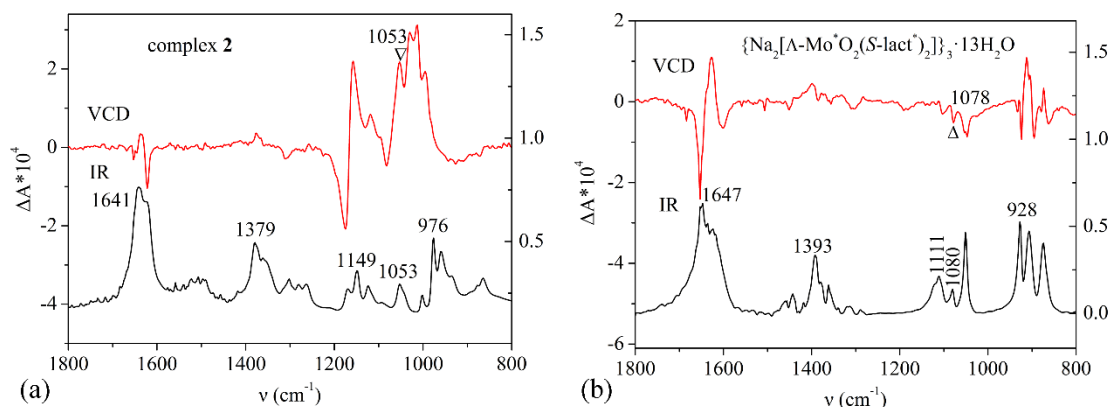
**Supplementary Fig. 10.** VCD and IR spectra of  $\{\text{Na}_2[\Delta\text{-Mo}^*\text{O}_2(\text{R-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  (a) and  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  (b) in the regions of 1800 – 800  $\text{cm}^{-1}$ .

**Analyses of VCD spectra.** The obtained VCD signals of a pair of enantiomers of deprotonated  $\{\text{Na}_2[\Delta\text{-Mo}^*\text{O}_2(\text{R-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  (a),  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  (b) were mirror images in the regions of 1800 – 800  $\text{cm}^{-1}$  as shown in Supplementary Fig. 10. The experimentally obtained VCD signals mostly agreed with the acquired IR signals simultaneously. VCD peaks at 1086  $\text{cm}^{-1}$  in  $\{\text{Na}_2[\Delta\text{-Mo}^*\text{O}_2(\text{R-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  and 1078  $\text{cm}^{-1}$  in  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  are assigned to the deprotonated C–O stretching vibrations based on the reported IR spectra of some alcohols and  $\alpha$ -hydroxycarboxylic acids.<sup>26</sup>



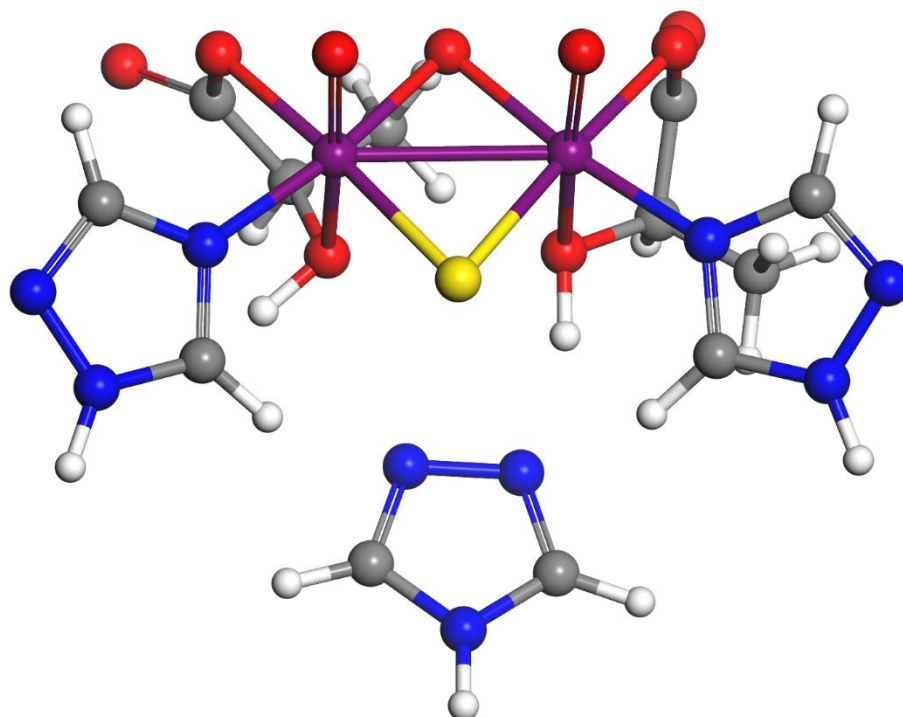
**Supplementary Fig. 11.** VCD and IR spectra of  $[\Delta/\Lambda\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**) and  $\{\text{Na}_2[\Delta\text{-Mo}^*\text{O}_2(R\text{-lact}^*)_2]\}_3\cdot 13\text{H}_2\text{O}$  using KBr pellet in the regions of 1800 – 800 cm<sup>-1</sup>.

**Analyses of VCD and IR spectra.** By contrast VCD and IR spectra of **1** and  $\{\text{Na}_2[\Delta\text{-Mo}^*\text{O}_2(R\text{-lact}^*)_2]\}_3\cdot 13\text{H}_2\text{O}$ , we can see  $\nu_{\text{as}}(\text{COO})$  peaks in them both appeared around 1650 cm<sup>-1</sup>,  $\nu_{\text{s}}(\text{COO})$  and  $\nu(\text{Mo=O})$  signals have about 10 wave number differences or more. The peaks around 1120 cm<sup>-1</sup> are identified as  $\nu(\text{C-N})$ . There will be some differences in the characteristic peaks of different compounds.

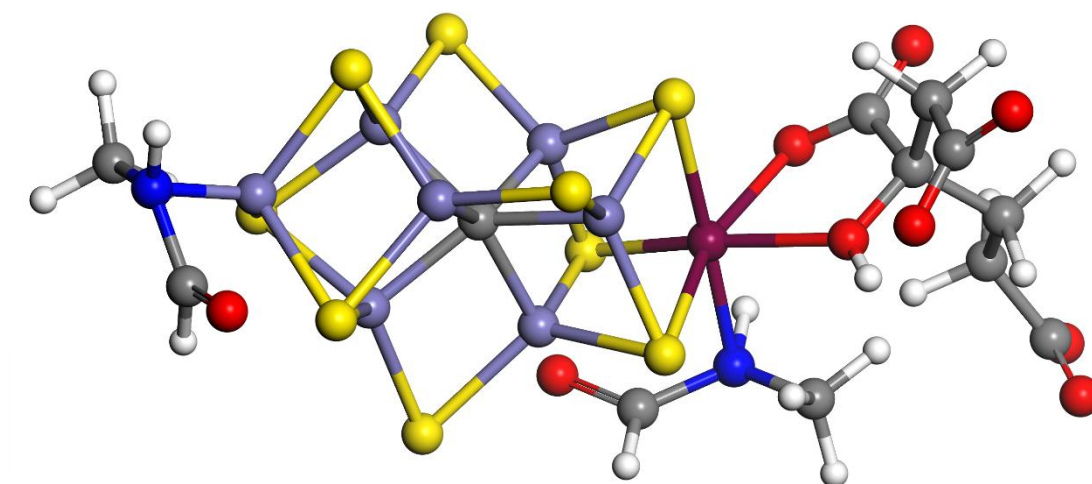


**Supplementary Fig. 12.** Comparisons of VCD and IR spectra of  $[\Lambda/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**, a) and  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$  (b) using KBr pellet in the regions of 1800 – 800  $\text{cm}^{-1}$ .

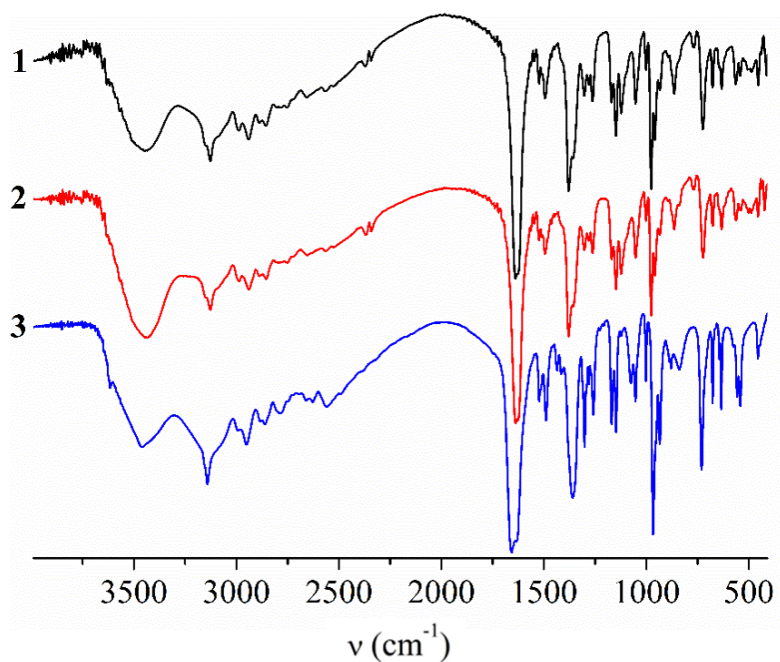
**Analyses of VCD and IR spectra.** By comparison Supplementary Fig. 12a with 12b, we can come to the same conclusion as the Supplementary Fig. 11 for similar  $\nu_{\text{as}}(\text{COO})$ ,  $\nu(\text{C-N})$  peaks, unlike  $\nu_{\text{s}}(\text{COO})$  and  $\nu(\text{Mo=O})$  signals in **2** and  $\{\text{Na}_2[\Lambda\text{-Mo}^*\text{O}_2(\text{S-lact}^*)_2]\}_3 \cdot 13\text{H}_2\text{O}$ .



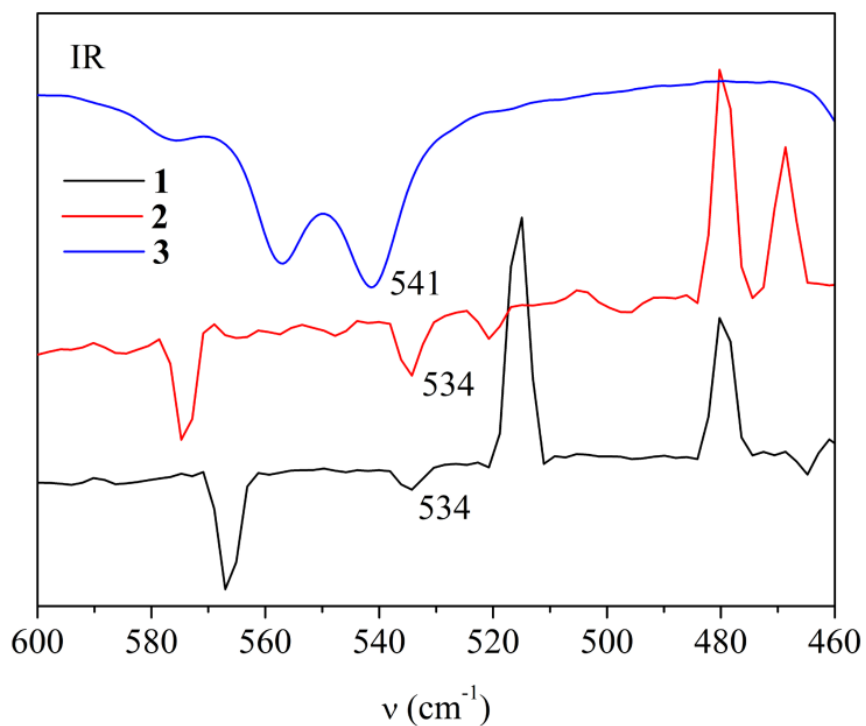
**Supplementary Fig. 13.** Optimized molecular structure of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**). Color: molybdenum, violet; oxygen, red; nitrogen, blue; carbon, gray; sulfur, yellow; hydrogen, white.



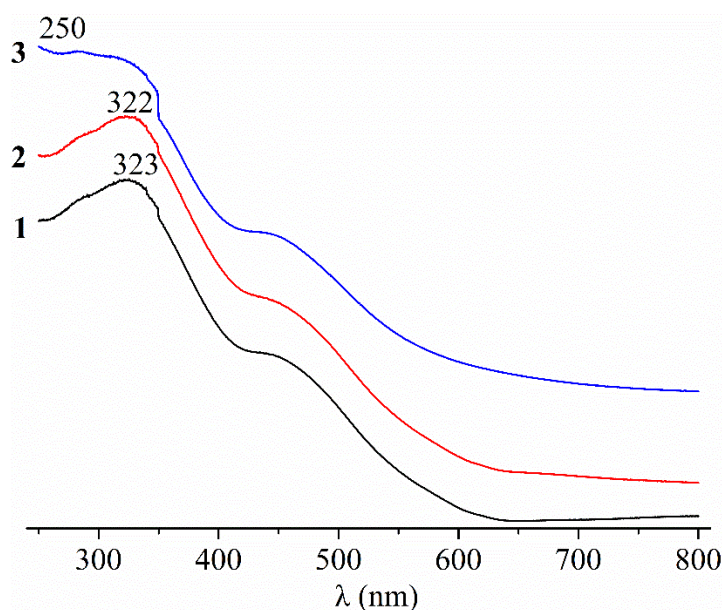
**Supplementary Fig. 14.** Optimized molecular structure of  $\Delta$ -Mo\*Fe<sub>7</sub>S<sub>9</sub>C[*R*-(H)homocit\*](NMF)<sub>2</sub> (**20**). Color: molybdenum, violet; oxygen, red; nitrogen, blue; carbon, gray; sulfur, yellow; hydrogen, white; iron, slate.



**Supplementary Fig. 15.** IR spectra of  
 $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  
 $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2),  
and  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3), in the region of 4000 ~ 450  $\text{cm}^{-1}$ .

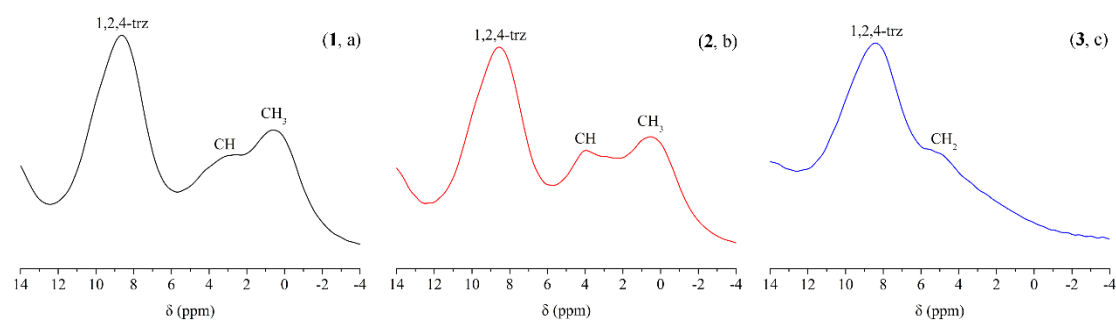


**Supplementary Fig. 16.** IR spectra of  $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2), and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3), in the region of 600 ~ 460  $\text{cm}^{-1}$ .



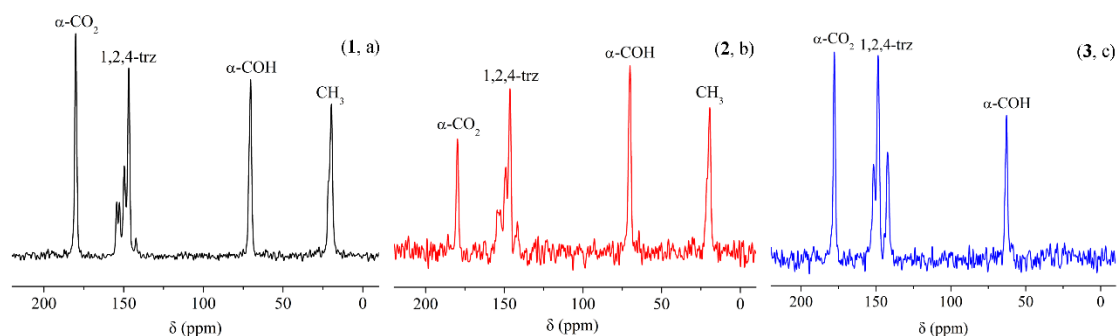
**Supplementary Fig. 17.** Solid diffused reflectance UV-Vis spectra of solids  $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**),  $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**), and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**).

**IR and UV spectroscopy analyses.** **1 ~ 3** have been characterized by IR spectroscopies. Based on the spectra shown in Supplementary Fig. 15, vibrations of asymmetric and symmetric coordinated carboxy groups appear at  $1655 \sim 1638 \text{ cm}^{-1}$  and  $1379 \sim 1359 \text{ cm}^{-1}$  respectively. The frequency differences  $\Delta[\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]^{27}$  are greater than  $200 \text{ cm}^{-1}$ , which are consistent with the monodentate coordinated carboxy group, and in agreement with **1 ~ 3** observed from X-ray structural analyses. The vibrations of  $\text{Mo}=\text{O}$  appear at  $977 \sim 967 \text{ cm}^{-1}$ . At lower frequencies, the IR bands  $534 \text{ cm}^{-1}$  in **1, 2** and  $541 \text{ cm}^{-1}$  in **3** are assigned to  $\text{Mo}-\text{O}$  vibrations which can be seen in Supplementary Fig. 16.<sup>20</sup> In UV-Vis spectra, strong absorption peaks are attribute to ligand-based  $\pi-\pi^*$  transitions and charge-transfer transition of  $\text{Mo}-\text{O}$  ( $250 \sim 323 \text{ nm}$  in **1 ~ 3**) as shown in Supplementary Fig. 17.



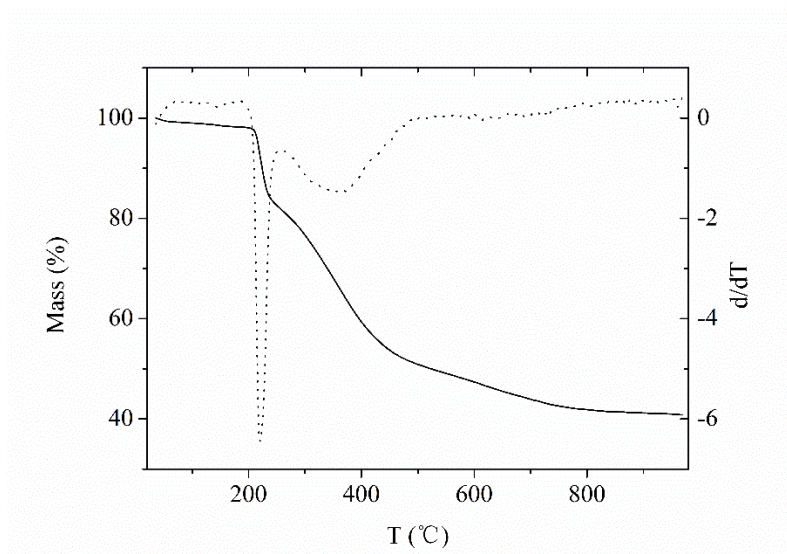
**Supplementary Fig. 18.** Solid-state  $^1\text{H}$  NMR spectra of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**, a),  $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**, b) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**, c).

**Solid  $^1\text{H}$  NMR spectroscopy analyses.** Solid  $^1\text{H}$  NMR spectra can provide valuable information for the coordination environments and chemical behaviors of new compounds **1** ~ **3** as shown in Supplementary Fig. 18. But the resolution of the solid  $^1\text{H}$  spectrum is poor, it is not easy to fit or calibrate and the characteristic peak curve is not sharp compared with  $^{13}\text{C}$  NMR spectra in Supplementary Fig. 19. The identification of the characteristic peaks in **1** ~ **3** have been listed in the synthetic section.

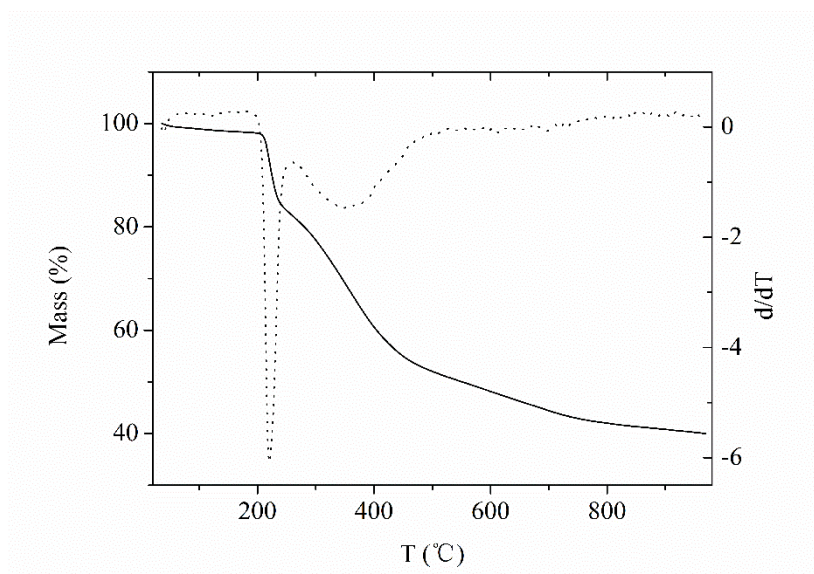


**Supplementary Fig. 19.** Solid-state  $^{13}\text{C}$  NMR spectra of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**, a),  $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**, b) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**, c).

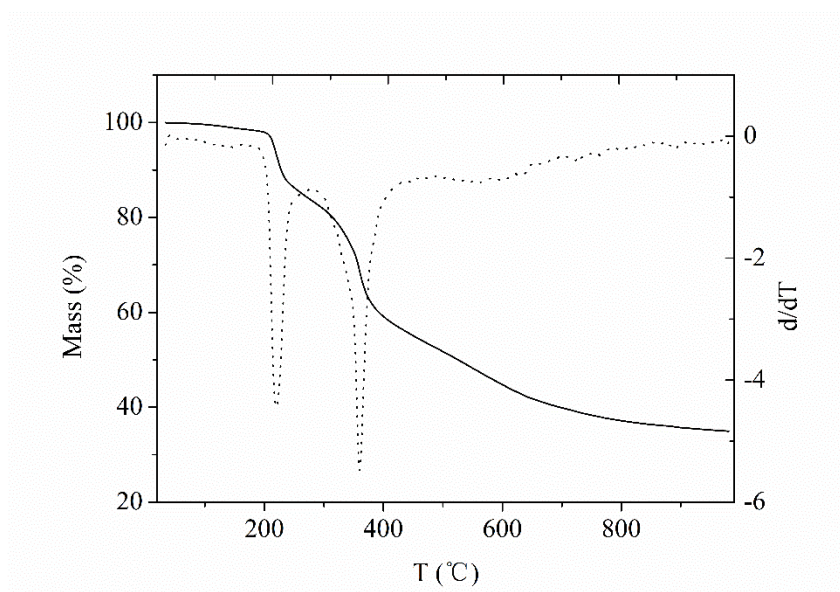
**Solid  $^{13}\text{C}$  NMR spectroscopy analyses.** Solid  $^{13}\text{C}$  NMR spectra provide valuable information for the coordination environments and chemical behaviors of **1** ~ **3** as shown in Supplementary Fig. 19. The coordinated  $\alpha\text{-CO}_2$  groups (180.11 ppm in **1**, 179.81 ppm in **2** and 177.87 ppm in **3**) and the coordinated  $\alpha$ -hydroxy groups (70.40 ppm in **1**, 70.17 ppm in **2** and 62.86 ppm in **3**) show obvious downfield shifts compared with free lactic acid ( $\alpha\text{-CO}_2$ , 176.18 ppm;  $\alpha\text{-CO}$ , 65.68 ppm) and glycolic acid ( $\alpha\text{-CO}_2$ , 177.04 ppm;  $\alpha\text{-CO}$ , 60.16 ppm) respectively. Due to the asymmetric coordination environments, 1,2,4-triazoles in **1** ~ **3** appear as multiple carbon signals (154.38 ~ 142.28 ppm in **1**, 154.50 ~ 141.69 ppm in **2** and 151.65 ~ 142.26 ppm in **3**). The coordinated triazoles also show obvious downfield shifts compared with free 1,2,4-triazole (146.91 ppm). However, attempt for the solid-state NMR spectrum of the extracted FeMo-co *via* long time superposition is unsuccessful due to strong paramagnetic effect.



**Supplementary Fig. 20a.** TG-DTG curves of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**).

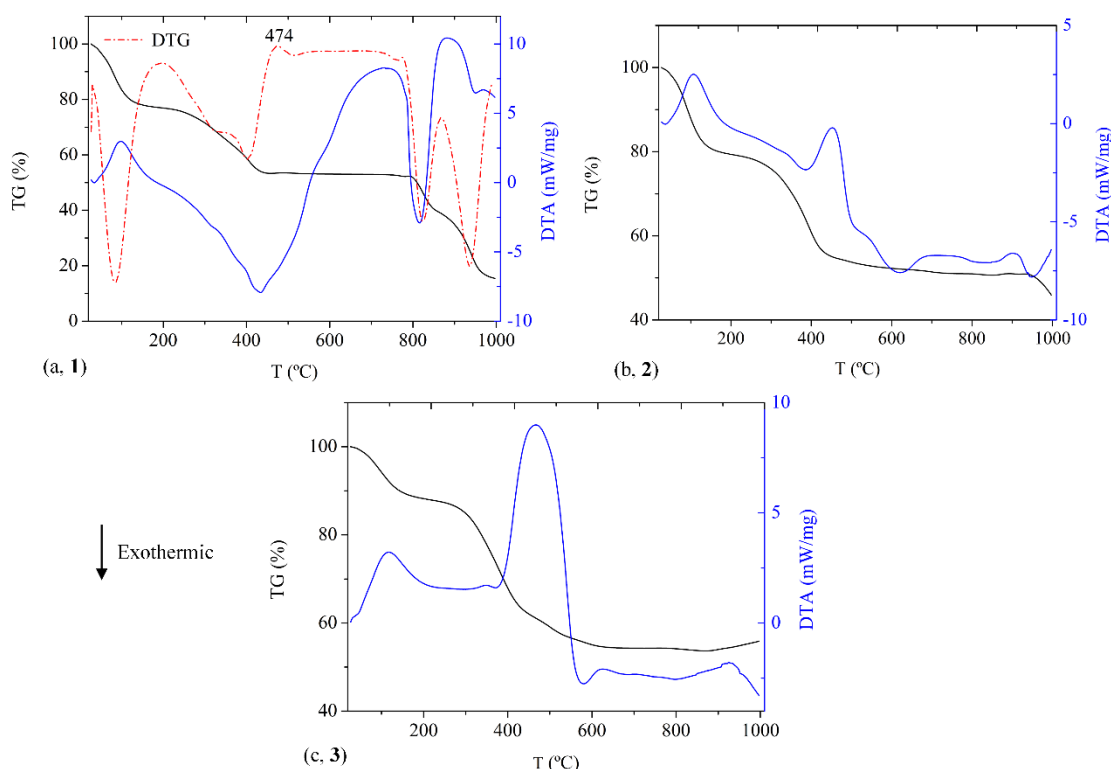


**Supplementary Fig. 20b.** TG-DTG curves of  $[\Lambda/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**).



**Supplementary Fig. 20c.** TG–DTG curves of  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**).

**TG analyses.** Thermal stabilities and decomposition patterns of **1** ~ **3** were investigated by thermogravimetric analyses. TG-DTG curves are shown in Supplementary Figs. 20a ~ 20c. Decompositions of anhydrous **1** ~ **3** occur at 220.3 °C, 220.3 °C and 220.1 °C respectively, which correspond to the weight losses of 1,2,4-triazoles. The mass % losses from 265 to 490 °C (31.80 % for **1**), 263 to 489 °C (26.71 % for **2**) and 276 to 451 °C (48.95 % for **3**) correspond to the mass % of C and H associated with the functionalized cations and anions respectively. The residues of **1** ~ **3** are molybdenum oxides.

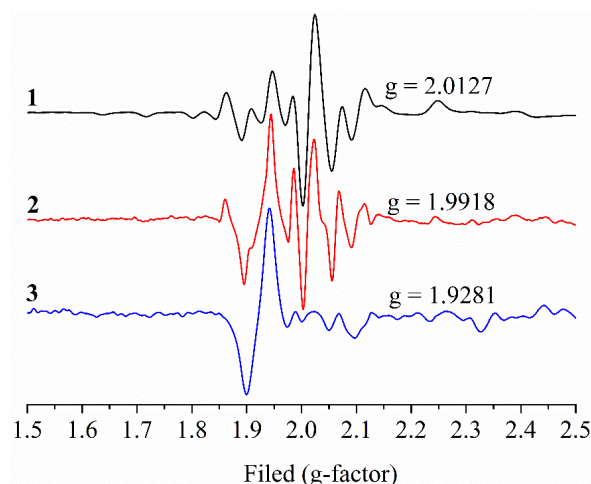


**Supplementary Fig. 21.** TG-DTA curves of  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1, a),  $[\Delta/\Delta\text{-Mo}^*\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2, b) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3, c).

**Differential Thermal analyses.** Thermal analysis (DTA/TG) was used to characterize thermal decomposition of the compounds and estimate melting point range.<sup>28</sup> The TG curve of compounds **1** ~ **3** indicates that those compounds do not melt and are stable up to 120 °C, at which temperature they begin to decompose. The transformation from powders into homogeneous oxide phase corresponds to two endothermic peaks in the DTA curves of **1** ~ **3** which are shown in Supplementary Fig. 21. The first one around 120 °C is related to remove of tiny water and the weight losses of 1,2,4-triazoles. The second peaks at 474 °C in **1**, 452 °C in **2** and 467 °C in **3** corresponds to decomposition reactions: change into the corresponding molybdenum oxides. Therefore, the melting point of **1** ~ **3** (actually decomposed into oxides) are approximately 474 °C, 452 °C, 467 °C respectively. Among them, the endothermic

peak at 474 °C in **1** can clearly see from the corresponding DTG curve (red).

Subsequent exothermic peaks may correspond to oxidation of evolved gas such as carbon monoxide.



**Supplementary Fig. 22.** X-bands of EPR spectra for  $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**),  $[\Delta/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (**2**) and  $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (**3**) in solid states at 90 K.

#### **Theoretical bond valence calculations and EPR spectroscopy analyses.**

Theoretical bond valence calculations give the valences of 5.214<sub>av</sub>, 5.206<sub>av</sub>, 5.224<sub>av</sub> for molybdenum atoms in **1** ~ **3** respectively, which can be seen in Supplementary Table 15. These are consistent with charge balance of +5 and further supported by electron paramagnetic resonance (EPR) experiment. As shown in Supplementary Fig. 22, the X-band EPR spectra of **1** ~ **3** exhibit  $S = \frac{1}{2}$  signals centered on  $g = 2.013$ , 1.992 and 1.928 at 90 K respectively, which are the feature of a  $4d^1$  metal center  $\text{Mo}^{5+}$ .<sup>29,30</sup> Moreover, the spectra of **1** and **2** show well-resolved hyperfine structures determined by  $^{95}\text{Mo}$  nuclear spin respectively.<sup>31</sup>

**Supplementary Table 1.** Crystallographic data and structural refinements for complexes [ $\Delta/\Lambda$ -Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(*R*-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)]·½H<sub>2</sub>O (**1**), [ $\Lambda/\Delta$ -Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(*S*-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)] (**2**), and [Mo<sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(Hglyc)<sub>2</sub>(trz)<sub>2</sub>(H<sub>2</sub>O)] (**3**).

|                                        | <b>1</b>                                                                          | <b>2</b>                                                                        | <b>3</b>                                                                        |
|----------------------------------------|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Empirical formula                      | C <sub>12</sub> H <sub>20</sub> Mo <sub>2</sub> N <sub>9</sub> O <sub>9.5</sub> S | C <sub>12</sub> H <sub>19</sub> Mo <sub>2</sub> N <sub>9</sub> O <sub>9</sub> S | C <sub>8</sub> H <sub>14</sub> Mo <sub>2</sub> N <sub>6</sub> O <sub>10</sub> S |
| Formula weight                         | 666.31                                                                            | 657.30                                                                          | 578.19                                                                          |
| Temperature/K                          | 100.01                                                                            | 100.00                                                                          | 193.0                                                                           |
| Crystal system                         | monoclinic                                                                        | monoclinic                                                                      | monoclinic                                                                      |
| Space group                            | <i>P</i> 2 <sub>1</sub>                                                           | <i>P</i> 2 <sub>1</sub>                                                         | <i>P</i> c                                                                      |
| <i>a</i> /Å                            | 12.3886(2)                                                                        | 12.3965(2)                                                                      | 10.9661(1)                                                                      |
| <i>b</i> /Å                            | 15.1481(2)                                                                        | 15.0742(3)                                                                      | 6.1069(6)                                                                       |
| <i>c</i> /Å                            | 12.4144(2)                                                                        | 12.4250(2)                                                                      | 13.3084(1)                                                                      |
| $\alpha$ /°                            | 90                                                                                | 90                                                                              | 90                                                                              |
| $\beta$ /°                             | 103.7620(1)                                                                       | 103.832(2)                                                                      | 104.846(1)                                                                      |
| $\gamma$ /°                            | 90                                                                                | 90                                                                              | 90                                                                              |
| Volume/Å <sup>3</sup>                  | 2262.85(6)                                                                        | 2254.50(7)                                                                      | 861.50(2)                                                                       |
| <i>Z</i>                               | 4                                                                                 | 4                                                                               | 2                                                                               |
| $\rho_{\text{calc}}$ /cm <sup>3</sup>  | 1.956                                                                             | 1.937                                                                           | 2.229                                                                           |
| $\mu$ /mm <sup>-1</sup>                | 10.554                                                                            | 10.566                                                                          | 1.643                                                                           |
| <i>F</i> (000)                         | 1324.0                                                                            | 1304.0                                                                          | 568.0                                                                           |
| Crystal size/mm <sup>3</sup>           | 0.2 × 0.1 × 0.02                                                                  | 0.14 × 0.1 × 0.05                                                               | 0.2 × 0.1 × 0.05                                                                |
| Radiation                              | CuK $\alpha$ ( $\lambda$ = 1.54184)                                               | CuK $\alpha$ ( $\lambda$ = 1.54184)                                             | MoK $\alpha$ ( $\lambda$ = 0.71073)                                             |
| 2 $\theta$ range for data collection/° | 7.332 to 155.646                                                                  | 7.328 to 136.468                                                                | 6.334 to 59.824                                                                 |
| Reflections collected                  | 9469                                                                              | 12325                                                                           | 3036                                                                            |

|                                               |                                  |                                  |                                  |
|-----------------------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Independent reflections                       | 9469                             | 6835                             | 3036                             |
| $R_{\text{sigma}}$                            | 0.0297                           | 0.0273                           | 0.0735                           |
| Data/restraints/parameters                    | 9469/22/618                      | 6835/360/616                     | 3036/11/251                      |
| Goodness of fit on $F^2$                      | 1.072                            | 1.030                            | 1.027                            |
| Final $R$ indexes [ $I > 2\sigma(I)$ ]        | $R_1 = 0.0465$ , $wR_2 = 0.1266$ | $R_1 = 0.0275$ , $wR_2 = 0.0741$ | $R_1 = 0.0411$ , $wR_2 = 0.0836$ |
| Final $R$ indexes [all data]                  | $R_1 = 0.0469$ , $wR_2 = 0.1270$ | $R_1 = 0.0280$ , $wR_2 = 0.0744$ | $R_1 = 0.0500$ , $wR_2 = 0.0882$ |
| Largest diff. peak/hole / e $\text{\AA}^{-3}$ | 1.67/-0.81                       | 1.00/-0.91                       | 1.05/-1.02                       |
| Flack parameter                               | 0.010(7)                         | 0.018(6)                         | -0.04(6)                         |

**Supplementary Table 2.** Selected hydrogen bond distances (Å) and angles (°) in  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**).

| Donor–H $\cdots$ Acceptor | D–H(Å)  | H $\cdots$ A(Å) | D $\cdots$ A(Å) | D–H $\cdots$ A(°) |
|---------------------------|---------|-----------------|-----------------|-------------------|
| O1–H1 $\cdots$ N8         | 0.86(4) | 2.53(4)         | 3.349(1)        | 161(3)            |
| O1–H1 $\cdots$ N9         | 0.86(4) | 1.89(6)         | 2.617(1)        | 141(1)            |
| O1w–H1w $\cdots$ O2       | 0.85    | 2.14            | 2.79(3)         | 133               |
| N3–H3 $\cdots$ O6a        | 0.88    | 2               | 2.792(1)        | 149               |
| N3–H3 $\cdots$ O15b       | 0.88    | 2.59            | 3.164(2)        | 124               |
| O4–H4 $\cdots$ N8         | 0.95    | 1.78            | 2.718(1)        | 171               |
| N6–H6 $\cdots$ O3c        | 0.88    | 1.86            | 2.704(1)        | 161               |
| N7–H7A $\cdots$ O17b      | 0.88    | 1.87            | 2.666(1)        | 150               |
| O10–H10A $\cdots$ N18     | 0.85(8) | 1.78(6)         | 2.574(2)        | 154(9)            |
| N12–H12 $\cdots$ O6       | 0.88    | 2.54            | 3.064(2)        | 119               |
| N12–H12 $\cdots$ O15c     | 0.88    | 1.95            | 2.787(1)        | 158               |
| O13–H13 $\cdots$ N17      | 0.85(3) | 1.84(3)         | 2.682(1)        | 169(2)            |
| N15–H15 $\cdots$ O12a     | 0.88    | 1.89            | 2.703(1)        | 153               |
| N16–H16 $\cdots$ O8       | 0.88    | 1.9             | 2.684(1)        | 148               |

Symmetry codes: (a)  $1 + x, y, z$ ; (b)  $1 + x, y, 1 + z$ ; (c)  $x, y, 1 + z$ . The value in brackets represents the error.

**Supplementary Table 3.** Selected hydrogen bond distances (Å) and angles (°) in  $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{S-Hlact}^*)_2(\text{trz})_2(\text{trz})](2)$ .

| Donor–H $\cdots$ Acceptor | D–H     | H $\cdots$ A | D $\cdots$ A | D–H $\cdots$ A |
|---------------------------|---------|--------------|--------------|----------------|
| O1–H1 $\cdots$ N9         | 0.85(3) | 1.88(3)      | 2.717(8)     | 169(3)         |
| N3–H3 $\cdots$ O6a        | 0.88    | 1.86         | 2.707(8)     | 160            |
| O4–H4 $\cdots$ N8         | 0.85(3) | 1.76(3)      | 2.609(7)     | 174(4)         |
| O4–H4 $\cdots$ N9         | 0.85(3) | 2.60(3)      | 3.345(7)     | 147(5)         |
| N6–H6 $\cdots$ O3b        | 0.88    | 2.02         | 2.820(7)     | 150            |
| N6–H6 $\cdots$ O12c       | 0.88    | 2.55         | 3.134(8)     | 125            |
| N7–H7A $\cdots$ O17c      | 0.88    | 1.9          | 2.700(7)     | 150            |
| O10–H10A $\cdots$ N18     | 0.85(2) | 1.83(2)      | 2.681(8)     | 172(6)         |
| N12–H12 $\cdots$ O15b     | 0.88    | 1.88         | 2.701(8)     | 154            |
| O13–H13 $\cdots$ N17      | 0.86(1) | 1.74(2)      | 2.566(9)     | 163(2)         |
| N15–H15 $\cdots$ O3       | 0.92(1) | 2.52(1)      | 3.048(8)     | 117(9)         |
| N15–H15 $\cdots$ O12a     | 0.92(1) | 1.93(1)      | 2.773(8)     | 151(1)         |
| N16–H16 $\cdots$ O8       | 0.88    | 1.91         | 2.686(7)     | 146            |

Symmetry codes: (a)  $x, y, -1 + z$ ; (b)  $-1 + x, y, z$ ; (c)  $-1 + x, y, -1 + z$ .

**Supplementary Table 4.** Selected hydrogen bond distances (Å) and angles (°) in [Mo<sub>2</sub>O<sub>2</sub>(μ<sub>2</sub>-S)(μ<sub>2</sub>-O)(Hglyc)<sub>2</sub>(trz)<sub>2</sub>(H<sub>2</sub>O)] (**3**).

| Donor–H ⋯ Acceptor | D–H     | H ⋯ A   | D ⋯ A    | D–H ⋯ A |
|--------------------|---------|---------|----------|---------|
| O1–H1 ⋯ O1wa       | 0.86(5) | 1.84(6) | 2.675(9) | 165(6)  |
| O1w–H1wA ⋯ O8b     | 0.87    | 1.82    | 2.670(9) | 166     |
| O1w–H1wB ⋯ O7      | 0.86    | 2.27    | 3.051(9) | 150     |
| N3–H3 ⋯ O6c        | 0.88    | 2.01    | 2.766(1) | 143     |
| O4–H4 ⋯ O1wa       | 0.86(6) | 1.83(6) | 2.675(9) | 167(3)  |
| N6–H6A ⋯ O3d       | 0.88    | 1.97    | 2.830(1) | 164     |

Symmetry codes: (a)  $x, 1 - y, -\frac{1}{2} + z$ ; (b)  $x, 2 - y, \frac{1}{2} + z$ ; (c)  $1 + x, 1 - y, \frac{1}{2} + z$ ; (d)  $-1 + x, -1 + y, z$ .

**Supplementary Table 5.** Selected bond distances (Å) and angles (°) for  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**).

| <b>1</b>   |           |             |           |
|------------|-----------|-------------|-----------|
| Mo2–Mo1    | 2.6752(9) | Mo4–Mo3     | 2.6975(1) |
| Mo2–S1     | 2.318(3)  | Mo4–S2      | 2.330(3)  |
| Mo2–O4     | 2.266(8)  | Mo4–O13     | 2.221(9)  |
| Mo2–O5     | 2.113(7)  | Mo4–O17     | 1.979(8)  |
| Mo2–O8     | 1.924(6)  | Mo4–O14     | 2.115(7)  |
| Mo2–N4     | 2.231(9)  | Mo4–N13     | 2.207(9)  |
| Mo2–O9     | 1.678(9)  | Mo4–O18     | 1.660(1)  |
| Mo1–S1     | 2.321(2)  | Mo3–S2      | 2.323(3)  |
| Mo1–O2     | 2.123(7)  | Mo3–O16     | 1.660(1)  |
| Mo1–O8     | 1.947(7)  | Mo3–O10     | 2.234(9)  |
| Mo1–O1     | 2.251(9)  | Mo3–O11     | 2.129(7)  |
| Mo1–O7     | 1.690(9)  | Mo3–O17     | 1.951(7)  |
| Mo1–N1     | 2.224(8)  | Mo3–N10     | 2.227(9)  |
|            |           |             |           |
| S1–Mo2–Mo1 | 54.84(6)  | O14–Mo4–O13 | 71.8(3)   |
| O4–Mo2–Mo1 | 98.3(2)   | O14–Mo4–N13 | 83.8(3)   |
| O4–Mo2–S1  | 87.0(2)   | N13–Mo4–Mo3 | 144.0(2)  |
| O5–Mo2–Mo1 | 129.4(2)  | N13–Mo4–S2  | 89.6(2)   |
| O5–Mo2–S1  | 157.0(2)  | N13–Mo4–O13 | 76.2(4)   |
| O5–Mo2–O4  | 70.2(3)   | O18–Mo4–Mo3 | 103.3(4)  |
| O5–Mo2–N4  | 83.5(3)   | O18–Mo4–S2  | 106.6(4)  |
| O8–Mo2–Mo1 | 46.63(2)  | O18–Mo4–O13 | 158.8(4)  |
| O8–Mo2–S1  | 99.3(2)   | O18–Mo4–O17 | 105.5(4)  |
| O8–Mo2–O4  | 87.9(3)   | O18–Mo4–O14 | 93.8(4)   |
| O8–Mo2–O5  | 83.1(3)   | O18–Mo4–N13 | 87.0(4)   |
| O8–Mo2–N4  | 162.7(3)  | S2–Mo3–Mo4  | 54.69(7)  |
| N4–Mo2–Mo1 | 143.8(2)  | O16–Mo3–Mo4 | 101.8(3)  |
| N4–Mo2–S1  | 89.0(2)   | O16–Mo3–S2  | 106.3(3)  |
| N4–Mo2–O4  | 77.2(3)   | O16–Mo3–O10 | 160.1(4)  |
| O9–Mo2–Mo1 | 100.7(3)  | O16–Mo3–O11 | 93.1(4)   |
| O9–Mo2–S1  | 106.1(3)  | O16–Mo3–O17 | 104.0(4)  |
| O9–Mo2–O4  | 160.8(3)  | O16–Mo3–N10 | 86.8(4)   |
| O9–Mo2–O5  | 95.5(4)   | O10–Mo3–Mo4 | 97.9(2)   |
| O9–Mo2–O8  | 103.3(4)  | O10–Mo3–S2  | 87.8(2)   |
| O9–Mo2–N4  | 88.8(4)   | O11–Mo3–Mo4 | 130.6(2)  |
| S1–Mo1–Mo2 | 54.74(6)  | O11–Mo3–S2  | 158.7(3)  |
| O2–Mo1–Mo2 | 129.5(2)  | O11–Mo3–O10 | 71.3(3)   |
| O2–Mo1–S1  | 157.4(2)  | O11–Mo3–N10 | 84.3(3)   |
| O2–Mo1–O1  | 70.6(3)   | O17–Mo3–Mo4 | 47.1(2)   |
| O2–Mo1–N1  | 83.9(3)   | O17–Mo3–S2  | 99.7(2)   |

|             |          |             |          |
|-------------|----------|-------------|----------|
| O8–Mo1–Mo2  | 45.93(2) | O17–Mo3–O10 | 87.0(4)  |
| O8–Mo1–S1   | 98.5(2)  | O17–Mo3–O11 | 83.7(3)  |
| O8–Mo1–O2   | 83.9(3)  | O17–Mo3–N10 | 164.3(4) |
| O8–Mo1–O1   | 85.7(3)  | N10–Mo3–Mo4 | 142.6(2) |
| O8–Mo1–N1   | 162.8(4) | N10–Mo3–S2  | 88.0(2)  |
| O1–Mo1–Mo2  | 96.4(2)  | N10–Mo3–O10 | 79.5(4)  |
| O1–Mo1–S1   | 87.1(2)  | Mo2–S1–Mo1  | 70.42(7) |
| O7–Mo1–Mo2  | 100.2(3) | Mo3–S2–Mo4  | 70.86(8) |
| O7–Mo1–S1   | 105.5(3) | C1–O2–Mo1   | 125.1(7) |
| O7–Mo1–O2   | 95.7(4)  | C5–O4–Mo2   | 118.9(7) |
| O7–Mo1–O8   | 103.4(4) | C14–O10–Mo3 | 119.2(7) |
| O7–Mo1–O1   | 162.9(3) | C4–O5–Mo2   | 124.8(7) |
| O7–Mo1–N1   | 90.0(4)  | C17–O13–Mo4 | 117.2(7) |
| N1–Mo1–Mo2  | 142.9(2) | C13–O11–Mo3 | 123.2(7) |
| N1–Mo1–S1   | 88.2(2)  | Mo2–O8–Mo1  | 87.4(3)  |
| N1–Mo1–O1   | 78.8(3)  | Mo3–O17–Mo4 | 86.7(3)  |
| S2–Mo4–Mo3  | 54.45(7) | C16–O14–Mo4 | 121.9(8) |
| O13–Mo4–Mo3 | 97.9(3)  | C2–O1–Mo1   | 120.6(6) |
| O13–Mo4–S2  | 86.5(2)  | C21–N13–Mo4 | 124.7(8) |
| O17–Mo4–Mo3 | 46.2(2)  | C22–N13–Mo4 | 133.5(7) |
| O17–Mo4–S2  | 98.6(2)  | C9–N4–Mo2   | 125.2(7) |
| O17–Mo4–O13 | 88.5(4)  | C10–N4–Mo2  | 129.6(8) |
| O17–Mo4–O14 | 82.8(3)  | C7–N1–Mo1   | 126.1(8) |
| O17–Mo4–N13 | 162.2(4) | C8–N1–Mo1   | 130.7(8) |
| O14–Mo4–Mo3 | 128.8(2) | C20–N10–Mo3 | 132.4(8) |
| O14–Mo4–S2  | 158.2(3) | C19–N10–Mo3 | 125.7(8) |

The value in brackets represents the error.

**Supplementary Table 6.** Selected bond distances (Å) and angles (°) for [Λ/Δ-Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>(μ<sub>2</sub>-S)(μ<sub>2</sub>-O)(S-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)] (2).

| 2          |           |             |           |
|------------|-----------|-------------|-----------|
| Mo2–Mo1    | 2.6719(6) | Mo4–Mo3     | 2.6961(6) |
| Mo2–S1     | 2.3248(1) | Mo4–S2      | 2.3245(2) |
| Mo2–O4     | 2.247(5)  | Mo4–O18     | 1.679(5)  |
| Mo2–O5     | 2.129(4)  | Mo4–O13     | 2.236(6)  |
| Mo2–O8     | 1.938(4)  | Mo4–O17     | 1.940(4)  |
| Mo2–O9     | 1.678(5)  | Mo4–O14     | 2.135(4)  |
| Mo2–N4     | 2.232(5)  | Mo4–N13     | 2.238(5)  |
| Mo1–S1     | 2.3240(2) | Mo3–S2      | 2.3341(2) |
| Mo1–O1     | 2.263(5)  | Mo3–O10     | 2.236(5)  |
| Mo1–O2     | 2.114(4)  | Mo3–O11     | 2.122(4)  |
| Mo1–O8     | 1.933(4)  | Mo3–O17     | 1.945(4)  |
| Mo1–O7     | 1.672(5)  | Mo3–O16     | 1.664(5)  |
| Mo1–N1     | 2.220(5)  | Mo3–N10     | 2.221(5)  |
|            |           |             |           |
| S1–Mo2–Mo1 | 54.90(4)  | O17–Mo4–Mo3 | 46.15(1)  |
| O4–Mo2–Mo1 | 96.72(1)  | O17–Mo4–S2  | 98.85(1)  |
| O4–Mo2–S1  | 87.01(1)  | O17–Mo4–O13 | 87.2(2)   |
| O5–Mo2–Mo1 | 129.69(1) | O17–Mo4–O14 | 84.62(2)  |
| O5–Mo2–S1  | 157.51(1) | O17–Mo4–N13 | 164.9(2)  |
| O5–Mo2–O4  | 70.83(2)  | O14–Mo4–Mo3 | 130.56(1) |
| O5–Mo2–N4  | 84.08(2)  | O14–Mo4–S2  | 158.40(2) |
| O8–Mo2–Mo1 | 46.27(1)  | O14–Mo4–O13 | 71.06(2)  |
| O8–Mo2–S1  | 98.74(1)  | O14–Mo4–N13 | 84.13(2)  |
| O8–Mo2–O4  | 85.24(2)  | N13–Mo4–Mo3 | 142.87(1) |
| O8–Mo2–O5  | 83.61(2)  | N13–Mo4–S2  | 88.08(1)  |
| O8–Mo2–N4  | 162.4(2)  | S2–Mo3–Mo4  | 54.47(4)  |
| O9–Mo2–Mo1 | 99.70(2)  | O10–Mo3–Mo4 | 98.80(1)  |
| O9–Mo2–S1  | 105.20(2) | O10–Mo3–S2  | 86.83(1)  |
| O9–Mo2–O4  | 163.24(2) | O11–Mo3–Mo4 | 128.63(1) |
| O9–Mo2–O5  | 95.8(2)   | O11–Mo3–S2  | 158.14(2) |
| O9–Mo2–O8  | 103.8(2)  | O11–Mo3–O10 | 71.34(2)  |
| O9–Mo2–N4  | 90.0(2)   | O11–Mo3–N10 | 83.89(2)  |
| N4–Mo2–Mo1 | 142.88(1) | O17–Mo3–Mo4 | 45.98(1)  |
| N4–Mo2–S1  | 87.98(1)  | O17–Mo3–S2  | 98.37(1)  |
| N4–Mo2–O4  | 78.8(2)   | O17–Mo3–O10 | 89.1(2)   |
| S1–Mo1–Mo2 | 54.93(4)  | O17–Mo3–O11 | 82.89(2)  |
| O1–Mo1–Mo2 | 98.05(1)  | O17–Mo3–N10 | 162.4(2)  |
| O1–Mo1–S1  | 86.42(1)  | O16–Mo3–Mo4 | 103.36(2) |
| O2–Mo1–Mo2 | 129.42(1) | O16–Mo3–S2  | 106.52(2) |
| O2–Mo1–S1  | 156.67(1) | O16–Mo3–O10 | 157.8(2)  |

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| O2–Mo1–O1   | 70.42(2)  | O16–Mo3–O11 | 94.0(2)   |
| O2–Mo1–N1   | 83.68(2)  | O16–Mo3–O17 | 105.8(2)  |
| O8–Mo1–Mo2  | 46.43(1)  | O16–Mo3–N10 | 86.7(3)   |
| O8–Mo1–S1   | 98.92(1)  | N10–Mo3–Mo4 | 144.10(1) |
| O8–Mo1–O1   | 87.33(2)  | N10–Mo3–S2  | 89.65(1)  |
| O8–Mo1–O2   | 83.25(2)  | N10–Mo3–O10 | 75.6(2)   |
| O8–Mo1–N1   | 162.6(2)  | Mo1–S1–Mo2  | 70.16(4)  |
| O7–Mo1–Mo2  | 100.40(2) | Mo4–S2–Mo3  | 70.72(4)  |
| O7–Mo1–S1   | 105.80(2) | C2–O1–Mo1   | 119.0(4)  |
| O7–Mo1–O1   | 161.45(2) | C1–O2–Mo1   | 124.2(4)  |
| O7–Mo1–O2   | 96.1(2)   | C5–O4–Mo2   | 120.4(4)  |
| O7–Mo1–O8   | 104.1(2)  | C14–O10–Mo3 | 118.3(4)  |
| O7–Mo1–N1   | 88.7(2)   | C17–O13–Mo4 | 119.6(4)  |
| N1–Mo1–Mo2  | 143.58(1) | C4–O5–Mo2   | 124.0(4)  |
| N1–Mo1–S1   | 88.65(2)  | C13–O11–Mo3 | 121.8(4)  |
| N1–Mo1–O1   | 77.4(2)   | Mo1–O8–Mo2  | 87.31(2)  |
| S2–Mo4–Mo3  | 54.80(4)  | Mo4–O17–Mo3 | 87.88(2)  |
| O18–Mo4–Mo3 | 101.76(2) | C16–O14–Mo4 | 123.4(4)  |
| O18–Mo4–S2  | 106.67(2) | C8–N1–Mo1   | 130.2(5)  |
| O18–Mo4–O13 | 160.0(2)  | C7–N1–Mo1   | 125.2(4)  |
| O18–Mo4–O17 | 103.8(2)  | C20–N10–Mo3 | 131.9(5)  |
| O18–Mo4–O14 | 93.0(2)   | C19–N10–Mo3 | 123.4(4)  |
| O18–Mo4–N13 | 86.8(2)   | C9–N4–Mo2   | 125.2(4)  |
| O13–Mo4–Mo3 | 97.93(1)  | C10–N4–Mo2  | 131.1(5)  |
| O13–Mo4–S2  | 87.75(1)  | C22–N13–Mo4 | 131.1(5)  |
| O13–Mo4–N13 | 79.7(2)   | C21–N13–Mo4 | 124.8(5)  |

**Supplementary Table 7.** Selected bond distances (Å) and angles (°) for [Mo<sub>2</sub>O<sub>2</sub>(μ<sub>2</sub>-S)(μ<sub>2</sub>-O)(Hglyc)<sub>2</sub>(trz)<sub>2</sub>(H<sub>2</sub>O)] (3).

| 3          |           |            |           |
|------------|-----------|------------|-----------|
| Mo1–Mo2    | 2.6672(9) | Mo2–S1     | 2.335(3)  |
| Mo1–S1     | 2.324(2)  | Mo2–O8     | 1.946(6)  |
| Mo1–O8     | 1.932(7)  | Mo2–O4     | 2.285(7)  |
| Mo1–O1     | 2.282(6)  | Mo2–N4     | 2.216(8)  |
| Mo1–O7     | 1.679(6)  | Mo2–O5     | 2.083(7)  |
| Mo1–O2     | 2.092(6)  | Mo2–O9     | 1.680(7)  |
| Mo1–N1     | 2.191(8)  |            |           |
|            |           |            |           |
| S1–Mo1–Mo2 | 55.28(7)  | O8–Mo2–O5  | 84.9(3)   |
| O8–Mo1–Mo2 | 46.77(2)  | O4–Mo2–Mo1 | 99.79(2)  |
| O8–Mo1–S1  | 98.7(2)   | O4–Mo2–S1  | 86.00(2)  |
| O8–Mo1–O1  | 85.1(3)   | N4–Mo2–Mo1 | 143.3(2)  |
| O8–Mo1–O2  | 85.0(3)   | N4–Mo2–S1  | 88.5(2)   |
| O8–Mo1–N1  | 162.2(3)  | N4–Mo2–O4  | 77.6(3)   |
| O1–Mo1–Mo2 | 98.18(2)  | O5–Mo2–Mo1 | 131.17(2) |
| O1–Mo1–S1  | 86.04(2)  | O5–Mo2–S1  | 156.61(2) |
| O7–Mo1–Mo2 | 98.5(2)   | O5–Mo2–O4  | 70.9(2)   |
| O7–Mo1–S1  | 105.8(2)  | O5–Mo2–N4  | 83.2(3)   |
| O7–Mo1–O8  | 104.5(3)  | O9–Mo2–Mo1 | 97.8(2)   |
| O7–Mo1–O1  | 163.1(3)  | O9–Mo2–S1  | 105.2(3)  |
| O7–Mo1–O2  | 95.8(3)   | O9–Mo2–O8  | 104.2(3)  |
| O7–Mo1–N1  | 89.6(3)   | O9–Mo2–O4  | 162.4(3)  |
| O2–Mo1–Mo2 | 131.7(2)  | O9–Mo2–N4  | 89.0(3)   |
| O2–Mo1–S1  | 156.35(2) | O9–Mo2–O5  | 96.5(3)   |
| O2–Mo1–O1  | 70.9(2)   | Mo1–S1–Mo2 | 69.83(7)  |
| O2–Mo1–N1  | 82.9(3)   | Mo1–O8–Mo2 | 86.9(3)   |
| N1–Mo1–Mo2 | 142.8(2)  | C2–O1–Mo1  | 116.7(5)  |
| N1–Mo1–S1  | 87.5(2)   | C4–O4–Mo2  | 118.3(5)  |
| N1–Mo1–O1  | 78.7(3)   | C1–O2–Mo1  | 125.7(6)  |
| S1–Mo2–Mo1 | 54.89(6)  | C8–N4–Mo2  | 133.9(6)  |
| O8–Mo2–Mo1 | 46.3(2)   | C7–N4–Mo2  | 122.4(7)  |
| O8–Mo2–S1  | 97.9(2)   | C3–O5–Mo2  | 126.4(6)  |
| O8–Mo2–O4  | 87.3(3)   | C6–N1–Mo1  | 128.7(7)  |
| O8–Mo2–N4  | 163.2(3)  | C5–N1–Mo1  | 127.2(7)  |

**Supplementary Table 8.** Detail calibrated adsorption data of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> for [ $\Lambda/\Delta$ -Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(S-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)] (2).

| Gases               |                   | O <sub>2</sub>       |                   | CO <sub>2</sub>      |                   | CH <sub>4</sub>      |                   | N <sub>2</sub>       |                   | H <sub>2</sub>       |  |
|---------------------|-------------------|----------------------|-------------------|----------------------|-------------------|----------------------|-------------------|----------------------|-------------------|----------------------|--|
| Temperature<br>(°C) | Pressure<br>(bar) | Adsorption<br>(mg/g) | Pressure<br>(bar) | Adsorption<br>(mg/g) | Pressure<br>(bar) | Adsorption<br>(mg/g) | Pressure<br>(bar) | Adsorption<br>(mg/g) | Pressure<br>(bar) | Adsorption<br>(mg/g) |  |
| 25.0                | 0                 | 0                    | 0                 | 0                    | 0                 | 0                    | 0                 | 0                    | 0                 | 0                    |  |
|                     | 1.890             | 1.7193               | 1.900             | 2.2802               | 1.900             | 0.3396               | 1.900             | 0.4301               | 1.920             | 0.1173               |  |
|                     | 3.894             | 2.9943               | 3.895             | 3.4581               | 3.900             | 0.4503               | 3.900             | 0.4771               | 3.900             | 0.0577               |  |
|                     | 5.900             | 4.2824               | 5.898             | 4.6204               | 5.898             | 0.4415               | 5.894             | 0.5740               | 5.897             | 0.0343               |  |
|                     | 7.897             | 5.6792               | 7.893             | 5.5768               | 7.896             | 0.4854               | 7.897             | 0.6348               | 7.902             | 0.1136               |  |
|                     | 9.897             | 6.9754               | 9.893             | 6.3254               | 9.896             | 0.5086               | 9.894             | 0.6016               | 9.903             | 0.0728               |  |
|                     | 11.897            | 8.0490               | 11.895            | 6.9945               | 11.897            | 0.4925               | 11.896            | 0.5992               | 11.911            | 0.0138               |  |
|                     | 13.896            | 9.2541               | 13.894            | 7.5706               | 13.899            | 0.5568               | 13.898            | 0.5114               | 13.908            | 0.0495               |  |
|                     | 15.893            | 10.4207              | 15.894            | 8.3032               | 15.894            | 0.6907               | 15.899            | 0.5800               | 15.910            | 0.0922               |  |
|                     | 17.896            | 11.7313              | 17.891            | 8.7941               | 17.898            | 0.6454               | 17.896            | 0.5411               | 17.907            | 0.0674               |  |
|                     | 19.895            | 12.8728              | 19.892            | 9.2422               | 19.896            | 0.5239               | 19.896            | 0.4152               | 19.909            | 0.0495               |  |
|                     | 21.896            | 14.1802              | 21.892            | 9.6216               | 21.898            | 0.4576               | 21.894            | 0.0658               | 21.904            | 0.1294               |  |
|                     | 23.897            | 15.4770              | 23.893            | 10.0777              | 23.898            | 0.3479               | 23.896            | 0.4547               | 23.908            | 0.1393               |  |
|                     | 25.896            | 16.6082              | 25.891            | 10.2523              | 25.897            | 0.3276               | 25.897            | 0.7008               | 25.904            | 0.1729               |  |
|                     | 27.896            | 17.6086              | 27.890            | 10.6862              | 27.897            | 0.2442               | 27.897            | 0.7190               | 27.908            | 0.1422               |  |
|                     | 29.894            | 19.2340              | 29.891            | 10.8411              | 29.897            | 0.2638               | 29.894            | 0.1340               | 29.905            | 0.1361               |  |

**Supplementary Table 9.** Detail calibrated adsorption data of O<sub>2</sub> and N<sub>2</sub> for [ $\Delta/\Lambda$ -Mo<sup>\*</sup><sub>2</sub>O<sub>2</sub>( $\mu_2$ -S)( $\mu_2$ -O)(R-Hlact<sup>\*</sup>)<sub>2</sub>(trz)<sub>2</sub>(trz)]·½H<sub>2</sub>O (**1**).

| Gases               | O <sub>2</sub>    |                      | N <sub>2</sub>    |                      |
|---------------------|-------------------|----------------------|-------------------|----------------------|
| Temperature<br>(°C) | Pressure<br>(bar) | Adsorption<br>(mg/g) | Pressure<br>(bar) | Adsorption<br>(mg/g) |
| 25.0                | 0                 | 0                    | 0                 | 0                    |
|                     | 1.890             | 1.4455               | 1.900             | 0.1980               |
|                     | 3.898             | 2.6793               | 3.890             | 0.2921               |
|                     | 5.894             | 3.8940               | 5.891             | 0.1725               |
|                     | 7.895             | 5.1682               | 7.900             | 0.2788               |
|                     | 9.897             | 6.0633               | 9.897             | 0.7341               |
|                     | 11.897            | 7.1437               | 11.896            | 0.3540               |
|                     | 13.894            | 8.5547               | 13.900            | 0.2062               |
|                     | 15.896            | 9.7397               | 15.897            | 0.2879               |
|                     | 17.895            | 10.8941              | 17.893            | 0.2162               |
|                     | 19.896            | 11.7403              | 19.896            | 0.2596               |
|                     | 21.896            | 13.1430              | 21.894            | 0.1519               |
|                     | 23.892            | 14.4176              | 23.894            | 0.0774               |
|                     | 25.893            | 15.2043              | 25.896            | 0.2977               |
|                     | 27.895            | 16.6807              | 27.894            | 0.3849               |
|                     | 29.895            | 17.6979              | 29.895            | 0.1193               |

**Supplementary Table 10.** Comparisons of selected bond distances (Å) for  
 $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  
 $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2),  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3),  $(\text{PyH})_2[\text{Mo}_2\text{O}_4(\text{glyc})_2\text{Py}_2]$  (4),<sup>1</sup>  
 $(\text{PyH})_4[\text{Mo}_4\text{O}_8\text{Cl}_4(\text{glyc})_2]\cdot 2\text{EtOH}$  (5),<sup>1</sup>  $[\text{Mo}_4\text{O}_8(\text{glyc})_2\text{Py}_4]$  (6),<sup>1</sup>  
 $\text{K}_6[(\text{MoO}_2)_8(\text{glyc})_6(\text{Hglyc})_2]\cdot 10\text{H}_2\text{O}$  (7),<sup>2</sup> *trans*- $[(\text{MoO})_2\text{O}(\text{glyc})_2(\text{bpy})_2]\cdot 3\text{H}_2\text{O}$  (8),<sup>3</sup>  
*trans*- $[(\text{MoO})_2\text{O}(\text{R,S-lact})_2(\text{bpy})_2]\cdot 3\text{H}_2\text{O}$  (9),<sup>3</sup>  
*trans*- $[(\text{MoO})_2\text{O}(\text{R,S-lact})_2(\text{phen})_2]\cdot 4\text{H}_2\text{O}$  (10),<sup>3</sup>  
 $\text{Na}_2[\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-O})_3(\text{glyc})_3(2\text{-mim})_3]\cdot 1.5\text{H}_2\text{O}$  (11),<sup>4</sup>  
 $(4\text{-Hmim})_6[\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-O})_3(\text{glyc})_3(4\text{-mim})_3]_2[\text{MoO}_2(\text{glyc})_2]$  (12),<sup>4</sup>  
 $\text{Na}_3(4\text{-Hmim})[\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-O})_3(\text{SO}_3)(\text{glyc})_3(4\text{-mim})]\cdot 8\text{H}_2\text{O}$  (13),<sup>4</sup>  
 $[\text{Mo}_3\text{SO}_3(\text{glyc})_2(\text{im})_5]\cdot \text{im}\cdot \text{H}_2\text{O}$  (14),<sup>5</sup>  $\text{Na}_2[\text{Mo}_3\text{SO}_3(\text{R,S-lact})_3(\text{im})_3]\cdot 10\text{H}_2\text{O}$  (15),<sup>5</sup>  
 $[\text{Mo}_3\text{S}_4(\text{PPh}_3)_3(\text{Hlact})_2(\text{lact})]$  (16),<sup>6</sup>  $\text{K}_2[\text{MoO}_2(\text{glyc})_2]\cdot \text{H}_2\text{O}$  (17),<sup>2</sup>  
 $[(\text{C}_6\text{H}_5)_4\text{P}][\text{MoO}_2(\text{glyc})(\text{Hglyc})]$  (18),<sup>1</sup>  $[\text{Na}_2[\text{MoO}_2(\text{S-lact})_2]]_3\cdot 13\text{H}_2\text{O}$  (19).<sup>2</sup>

| Complexes | Mo–O <sub>α</sub> -hydroxy         | Mo–O <sub>α</sub> -carboxy | C–O <sub>α</sub> -hydroxy         |
|-----------|------------------------------------|----------------------------|-----------------------------------|
| Mo(V)     |                                    |                            |                                   |
| <b>1</b>  | 2.251(9)                           | 2.123(7)                   | 1.426(1)                          |
|           | 2.266(8)                           | 2.113(7)                   | 1.390(2)                          |
|           | 2.221(9)                           | 2.115(7)                   | 1.433(1)                          |
|           | 2.234(9)                           | 2.129(7)                   | 1.427(1)                          |
|           | 2.236(5)                           | 2.122(4)                   | 1.418(8)                          |
| <b>2</b>  | 2.236(6)                           | 2.135(4)                   | 1.436(8)                          |
|           | 2.247(5)                           | 2.129(4)                   | 1.425(7)                          |
|           | 2.263(5)                           | 2.114(4)                   | 1.413(8)                          |
| <b>3</b>  | 2.285(7)                           | 2.083(7)                   | 1.418(1)                          |
|           | 2.282(6)                           | 2.092(6)                   | 1.443(1)                          |
| average   | 2.252(7)                           | 2.116(6)                   | 1.423(4)                          |
|           | Mo–O <sub>α</sub> -alkoxy          | Mo–O <sub>α</sub> -carboxy | C–O <sub>α</sub> -alkoxy          |
| <b>4</b>  | 2.183(2)                           | 2.092(2)                   | 1.420(3)                          |
| <b>5</b>  | 2.245(3)/2.115(2)                  | 2.117(3)                   | 1.424(5)                          |
| <b>6</b>  | 2.183(3)/2.097(3)                  | 2.046(3)                   | 1.419(5)                          |
| <b>7</b>  | 1.984(7)                           |                            |                                   |
|           | 2.073(5)/2.182(5)                  | 2.064(6) <sub>av</sub>     | 1.408(1) <sub>av</sub>            |
|           | 2.130(5)/2.089(5)                  |                            |                                   |
| average   | 2.122(4)                           | 2.076(4)                   | 1.417(4)                          |
| <b>8</b>  | 1.958(3) <sub>av</sub>             | 2.067(4) <sub>av</sub>     | 1.417(6) <sub>av</sub>            |
| <b>9</b>  | 1.953(6) <sub>av</sub>             | 2.051(7) <sub>av</sub>     | 1.415(1) <sub>av</sub>            |
| <b>10</b> | 1.958(2) <sub>av</sub>             | 2.064(2) <sub>av</sub>     | 1.405(4) <sub>av</sub>            |
| average   | 1.956(4)                           | 2.061(5)                   | 1.412(4)                          |
|           | Mo–O <sub>α</sub> -hydroxy/hydroxy | Mo–O <sub>α</sub> -carboxy | C–O <sub>α</sub> -hydroxy/hydroxy |
| Mo(IV)    |                                    |                            |                                   |
| <b>11</b> | 2.003(5) <sub>av</sub>             | 2.172(6) <sub>av</sub>     | 1.409(1) <sub>av</sub>            |
| <b>12</b> | 2.011(3) <sub>av</sub>             | 2.138(4) <sub>av</sub>     | 1.414(7) <sub>av</sub>            |
| <b>13</b> | 2.016(2) <sub>av</sub>             | 2.143(2) <sub>av</sub>     | 1.412(4) <sub>av</sub>            |
| <b>14</b> | 1.986(2) <sub>av</sub>             | 2.127(2) <sub>av</sub>     | 1.397(5) <sub>av</sub>            |

|           |                                 |                                 |                                 |
|-----------|---------------------------------|---------------------------------|---------------------------------|
| <b>15</b> | 1.999(7) <sub>av</sub>          | 2.133(6) <sub>av</sub>          | 1.42(2) <sub>av</sub>           |
| <b>16</b> | 2.092(3)/2.204(4) <sub>av</sub> | 2.083(4)/2.118(4) <sub>av</sub> | 1.299(7)/1.422(8) <sub>av</sub> |
| average   | 2.018(4)/2.204(4)               | 2.133(4)/2.118(4)               | 1.392(4)/1.422(8)               |
| Mo(VI)    |                                 |                                 |                                 |
| <b>17</b> | 1.941(2) <sub>av</sub>          | 2.203(3) <sub>av</sub>          | 1.404(5) <sub>av</sub>          |
| <b>18</b> | 1.945(1)                        | 2.271(1)                        | 1.392(2)                        |
| <b>19</b> | 1.958(5) <sub>av</sub>          | 2.191(5) <sub>av</sub>          | 1.425(8) <sub>av</sub>          |
| average   | 1.948(3)                        | 2.222(3)                        | 1.407(5)                        |

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**Supplementary Table 11.** The bond distances (Å) of Mo–O $_{\alpha}$ -alkoxy/hydroxy, Mo–O $_{\alpha}$ -carboxy and C–O $_{\alpha}$ -alkoxy/hydroxy in FeMo-cos of nitrogenases (**20**).

| PDB ID                                       | Resolutions | Mo–O $_{\alpha}$ -alkoxy/ $\alpha$ -hy<br>droxy | Mo–O $_{\alpha}$ -carboxy | C–O $_{\alpha}$ -alkoxy/ $\alpha$ -hydr<br>oxy |
|----------------------------------------------|-------------|-------------------------------------------------|---------------------------|------------------------------------------------|
| 36 structures of FeMo-cofactors <sup>5</sup> |             | 2.272 <sub>av</sub>                             | 2.263 <sub>av</sub>       | 1.449 <sub>av</sub>                            |
| 6CDK <sup>32</sup>                           | 2.1 Å       | 1.949, 1.936                                    | 1.989, 1.966              | 1.449, 1.451                                   |
| 6O7L <sup>33</sup>                           | 2.26 Å      | 2.492, 2.367                                    | 2.371, 2.459              | 1.433, 1.432                                   |
| 6O7M <sup>33</sup>                           | 1.4 Å       | 2.187, 2.241                                    | 2.208, 2.194              | 1.437, 1.436                                   |
| 6O7N <sup>33</sup>                           | 1.75 Å      | 2.211, 2.299                                    | 2.275, 2.194              | 1.425, 1.442                                   |
| 6O7O <sup>33</sup>                           | 1.89 Å      | 2.231, 2.268                                    | 2.249, 2.244              | 1.442, 1.430                                   |
| 6O7P <sup>33</sup>                           | 1.7 Å       | 2.340, 2.295                                    | 2.272, 2.290              | 1.435, 1.445                                   |
| 6O7Q <sup>33</sup>                           | 2 Å         | 2.390, 2.377                                    | 2.386, 2.366              | 1.435, 1.437                                   |
| 6O7R <sup>33</sup>                           | 2.27 Å      | 2.303, 2.371                                    | 2.421, 1.765              | 1.440, 1.438                                   |
| 6O7S <sup>33</sup>                           | 2.27 Å      | 2.389, 2.324                                    | 2.438, 2.419              | 1.430, 1.427                                   |
| 6OP1 <sup>34</sup>                           | 1.7 Å       | 2.261, 2.243                                    | 2.235, 2.204              | 1.439, 1.446                                   |
| 6OP2 <sup>34</sup>                           | 1.9 Å       | 2.274, 2.002                                    | 2.212, 2.156              | 1.450, 1.446                                   |
| 6OP3 <sup>34</sup>                           | 1.6 Å       | 2.216, 2.215                                    | 2.172, 2.174              | 1.436, 1.439                                   |
| 6OP4 <sup>34</sup>                           | 2.3 Å       | 2.137, 2.220                                    | 2.217, 2.184              | 1.446, 1.450                                   |
| Average                                      |             | 2.263                                           | 2.250                     | 1.445                                          |

**Bond distances comparison.** Comparisons of selected bond distances (Å) for oxidomolybdenum(V) lactates and glycolates **1** ~ **3** and the other molybdenum(IV/V/VI) lactates, glycolates **4** ~ **19** are shown in Supplementary Tables 5 ~ 7 and 10 ~ 11 respectively. The protonated Mo(V)–O $_{\alpha}$ -hydroxy distances [2.252(7)<sub>av</sub> Å] in **1** ~ **3** are obviously longer than Mo(V)–O $_{\alpha}$ -alkoxy distances [2.183(2) Å] in **4** in identical coordination mode, and longer than Mo(V)–O $_{\alpha}$ -alkoxy distances in **5** ~ **7** [2.122(4)<sub>av</sub> Å] in multi-cores of oxidomolybdenum glycolates. We can also found that Mo–O $_{\alpha}$ -alkoxy distances [1.958(3)<sub>av</sub> Å] in **8**, [1.956(4)<sub>av</sub> Å] in **9** ~ **10** are significantly reduced in bridged monooxy coordination mode compared with other coordination pattern simultaneously. Similarly, we can observe the protonated Mo(IV)–O $_{\alpha}$ -hydroxy distances in **16** [2.204(4)<sub>av</sub> Å] are longer than Mo(IV)–O $_{\alpha}$ -alkoxy distances in **11** ~ **16** [2.018(4)<sub>av</sub> Å], this indicates that protonation can lengthen the Mo–O distance and is common over 2.2 Å. The Mo(IV)–O $_{\alpha}$ -alkoxy distances in **11** ~ **16** [2.018(4)<sub>av</sub> Å] are

longer than Mo(V)–O $_{\alpha}$ -alkoxy distances in **8** ~ **10** [1.956(4)<sub>av</sub> Å] and Mo(VI)–O $_{\alpha}$ -alkoxy distances in **17** ~ **19** [1.948(3)<sub>av</sub> Å], this implied that the lower valence state of the metal Mo resulted in longer Mo–O $_{\alpha}$ -alkoxy bond distances. When O $_{\alpha}$ -alkoxy coordinated with two molybdenum atoms, the Mo–O $_{\alpha}$ -alkoxy distances increased (**4** ~ **7**). The protonated Mo(V)–O $_{\alpha}$ -hydroxy distances [2.252(7)<sub>av</sub> Å] are closer to the average value of Mo–O distances in FeMo-cofactors (**20**) [2.263<sub>av</sub> Å] of FeMo-proteins, as obtained from protein data bank in Supplementary Table 11. This supports that the oxygen atom in Mo–O $_{\alpha}$ -alkoxy should be protonated in FeMo-co.

The Mo(V)–O $_{\alpha}$ -carboxy distances [2.116(6)<sub>av</sub> Å] observed in **1** ~ **3** are longer than those of molybdenum(V) complexes **4** [2.092(2) Å], **5** ~ **7** [2.076(4)<sub>av</sub> Å], **8** ~ **10** [2.061(4)<sub>av</sub> Å], these are mainly attributed to the effects of protonation. The Mo(IV)–O $_{\alpha}$ -carboxy distances [2.133(4)<sub>av</sub> Å] in complexes **11** ~ **16** were longer than those [2.092(2)<sub>av</sub> Å] in molybdenum (V) complexes **4**, **5** ~ **7** [2.076(4)<sub>av</sub> Å] and **8** ~ **10** [2.061(5)<sub>av</sub> Å] owing to the influence of the metal valence, but shorter than those in **17** ~ **19** [2.222(3)<sub>av</sub> Å]. This might be due to the *trans*-effect. Unlike the Mo–O $_{\alpha}$ -alkoxy/hydroxy bond distances, the Mo–O $_{\alpha}$ -carboxy distances [2.116(6)<sub>av</sub> Å] showed no major difference to the average value of FeMo-cofactors [**20**, 2.250 Å].

Furthermore, the C–O $_{\alpha}$ -hydroxy distances [1.423(4)<sub>av</sub> Å] in **1** ~ **3** are little longer than complexes **5** ~ **7** [1.417(4)<sub>av</sub> Å], **8** ~ **10** [1.412(4)<sub>av</sub> Å], but closer to protonated **16** [1.422(8) Å], and significantly longer than Mo(IV) complexes **11** ~ **16** [1.392(4)<sub>av</sub> Å], Mo(VI) complexes **17** ~ **19** [1.407(5)<sub>av</sub> Å], loser to the average value in FeMo-cos [**20**, 1.445<sub>av</sub> Å]. So the Mo(IV/V/VI)–O $_{\alpha}$ -alkoxy/hydroxy bond is greatly affected by protonation and affect the neighboring C–O bond strength. Excluding the influence of oxidation state(Mo), the Mo(V)–O $_{\alpha}$ -hydroxy, Mo(V)–O $_{\alpha}$ -carboxy, and C–O $_{\alpha}$ -hydroxy distances in **1** ~ **3** all closer to FeMo-cos, supporting the fact that the oxygen atom

involved in Mo–O <sub>$\alpha$ -alkoxy</sub> coordination in FeMo-co should be protonated.

**Supplementary Table 12.** Qualitative assignments of the most intensive bands in VCD spectra of FeMo-co **20** and  $K_5[\Lambda, \Lambda, \Lambda, \Lambda\text{-Mo}^*_4\text{O}_{11}(\text{R-Hhomocit}^*)_2]\text{Cl}\cdot 5\text{H}_2\text{O}$  **21**.

| <b>20</b>  | frequency assignments (cm <sup>-1</sup> ) | <b>21</b>  | frequency assignments (cm <sup>-1</sup> )     |
|------------|-------------------------------------------|------------|-----------------------------------------------|
| 1657       | $\nu_{\text{as}}(\text{CO}_2^-)$          | 1705       | $\nu_{\text{as}}(\gamma\text{-CO}_2\text{H})$ |
|            |                                           | 1616       | $\nu_{\text{as}}(\text{CO}_2^-)$              |
| 1622       | $\nu_{\text{as}}(\text{CO}_2^-)$          |            |                                               |
| 1608       | $\nu_{\text{as}}(-\text{NHCO})$           |            |                                               |
| 1527       | NMF                                       |            |                                               |
| 1479, 1383 | $\nu_{\text{s}}(\text{CO}_2^-)$           | 1417, 1396 | $\nu_{\text{s}}(\text{CO}_2^-)$               |
| 1327       | $\nu_{\text{s}}(-\text{NHCO})$            |            |                                               |
| 1429       | NMF                                       |            |                                               |
| 1271       | NMF                                       |            |                                               |
| 1189       | $\nu(\text{C-C})$                         | 1180       | $\nu(\text{C-C})$                             |
| 1153       | $\nu(\text{C-C})$                         | 1157       | $\nu(\text{C-C})$                             |
| 1068       | $\nu(\text{C-O}_\text{H})$                | 1084       | $\nu(\text{C-O})$                             |
| 957        | —                                         | 953        | $\nu(\text{Mo=O})$                            |

Asymmetric and symmetric vibrations have been abbreviated as  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  respectively.

**Supplementary Table 13.** Comparison of obtained experimental IR, VCD characteristic signals of  $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (**1**) in the solid state and assignments of calculated VCD signals from optimized structure of **1**.

| <b>1</b>                      | IR<br>frequency (cm <sup>-1</sup> ) | Experimental<br>frequency (cm <sup>-1</sup> ) | Theoretical<br>frequency (cm <sup>-1</sup> ) |
|-------------------------------|-------------------------------------|-----------------------------------------------|----------------------------------------------|
| $\nu_{\text{as}}(\text{COO})$ | 1641                                | 1653                                          | 1672                                         |
| $\nu_{\text{s}}(\text{COO})$  | 1379                                | 1371                                          | 1352                                         |
| $\nu(\text{Mo=O})$            | 960 ~ 976                           | 959 ~ 976                                     | 989                                          |
| $\nu(\text{C-N})$             | 1148 ~ 1171                         | 1155 ~ 1180                                   | 1202 ~ 1213                                  |
| $\nu(\text{C-O}_\text{H})$    | 1053                                | 1051                                          | 1054                                         |

**Supplementary Table 14.** Comparisons of obtained experimental IR, VCD characteristic signals of extracted FeMo-co  $\Delta$ -Mo<sup>\*</sup>Fe<sub>7</sub>S<sub>9</sub>C[R-(H)homocit<sup>\*</sup>](NMF)<sub>2</sub> (**20**) and assignments of calculated VCD signals from optimized structure of **20**.

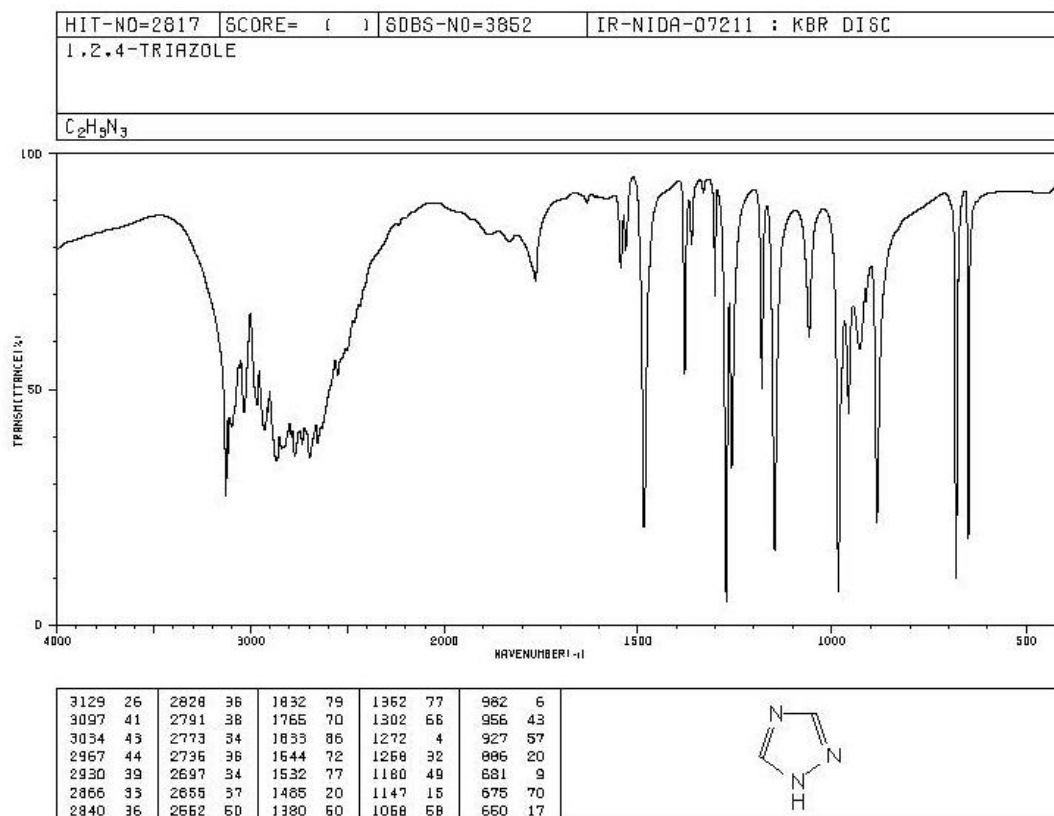
| <b>20</b>                         | IR<br>frequency (cm <sup>-1</sup> ) | Experimental<br>frequency (cm <sup>-1</sup> ) | Theoretical<br>frequency (cm <sup>-1</sup> ) |
|-----------------------------------|-------------------------------------|-----------------------------------------------|----------------------------------------------|
| $\nu_{\text{as}}(\text{CO}_2^-)$  | 1674, 1608                          | 1657, 1622                                    | 1655                                         |
| $\nu_{\text{s}}(\text{CO}_2^-)$   | 1483, 1400                          | 1479, 1383                                    | 1463, 1376                                   |
| NMF                               | 1425                                | 1429                                          | 1412                                         |
| $\nu(\text{C}-\text{C})$          | 1184                                | 1189                                          | 1178                                         |
| $\nu(\text{C}-\text{C})$          | 1163                                | 1153                                          | 1165                                         |
| $\nu(\text{C}-\text{O}_\text{H})$ | 1063                                | 1068                                          | 1058                                         |
| —                                 | 984                                 | 957                                           | 945                                          |

**Supplementary Table 15.** Bond valence calculations for complexes  
 $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$  (1),  
 $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$  (2), and  
 $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$  (3).

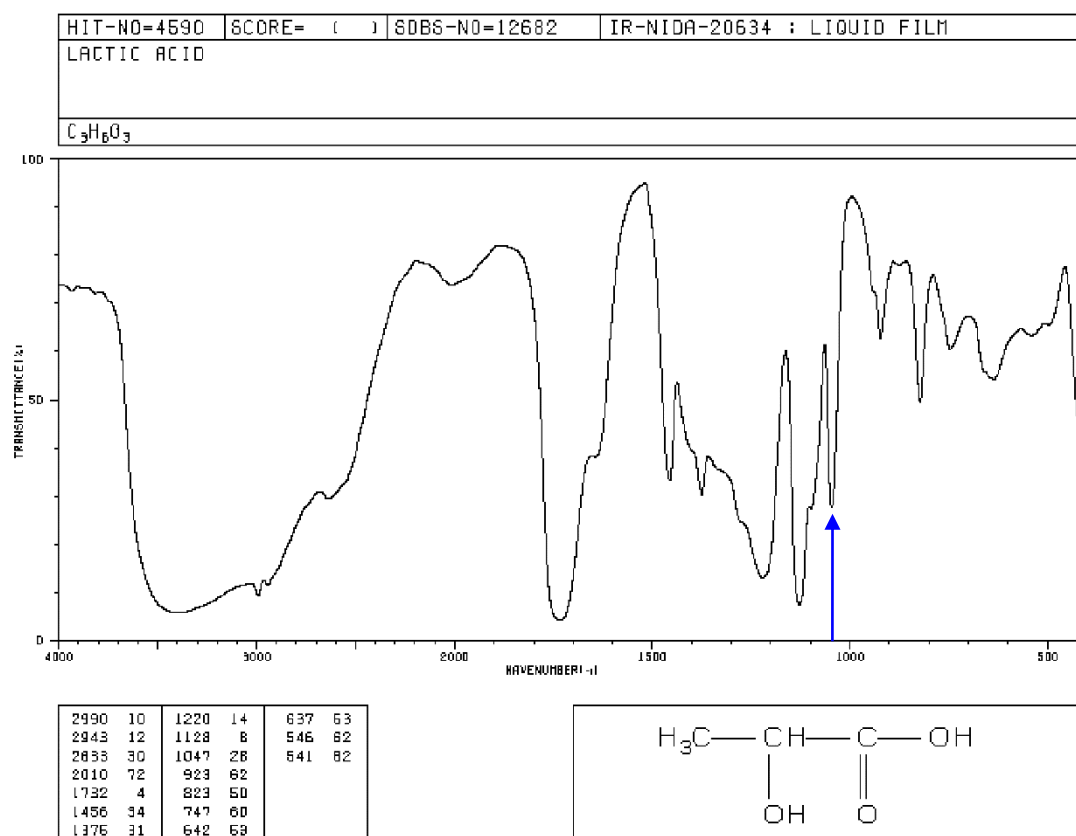
| Complexes                                                                                                                                                      | Atoms                  | N         | $\sum S_{ij}$             | $\Delta$                  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|-----------|---------------------------|---------------------------|
| $[\Delta/\Lambda\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(R\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]\cdot\frac{1}{2}\text{H}_2\text{O}$ (1) | Mo(1)                  | 5+        | 5.122                     | 0.122                     |
|                                                                                                                                                                | Mo(2)                  | 5+        | 5.229                     | 0.229                     |
|                                                                                                                                                                | Mo(3)                  | 5+        | 5.267                     | 0.267                     |
|                                                                                                                                                                | Mo(4)                  | 5+        | 5.239                     | 0.239                     |
|                                                                                                                                                                | <b>Mo<sub>av</sub></b> | <b>5+</b> | <b>5.214<sub>av</sub></b> | <b>0.214<sub>av</sub></b> |
| $[\Lambda/\Delta\text{-Mo}^*_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(S\text{-Hlact}^*)_2(\text{trz})_2(\text{trz})]$ (2)                                   | Mo(1)                  | 5+        | 5.243                     | 0.243                     |
|                                                                                                                                                                | Mo(2)                  | 5+        | 5.169                     | 0.169                     |
|                                                                                                                                                                | Mo(3)                  | 5+        | 5.249                     | 0.249                     |
|                                                                                                                                                                | Mo(4)                  | 5+        | 5.164                     | 0.164                     |
|                                                                                                                                                                | <b>Mo<sub>av</sub></b> | <b>5+</b> | <b>5.206<sub>av</sub></b> | <b>0.206<sub>av</sub></b> |
| $[\text{Mo}_2\text{O}_2(\mu_2\text{-S})(\mu_2\text{-O})(\text{Hglyc})_2(\text{trz})_2(\text{H}_2\text{O})]$ (3)                                                | Mo(1)                  | 5+        | 5.276                     | 0.276                     |
|                                                                                                                                                                | Mo(2)                  | 5+        | 5.172                     | 0.172                     |
|                                                                                                                                                                | <b>Mo<sub>av</sub></b> | <b>5+</b> | <b>5.224<sub>av</sub></b> | <b>0.224<sub>av</sub></b> |

Average has been abbreviated as av, bold represents the average result.

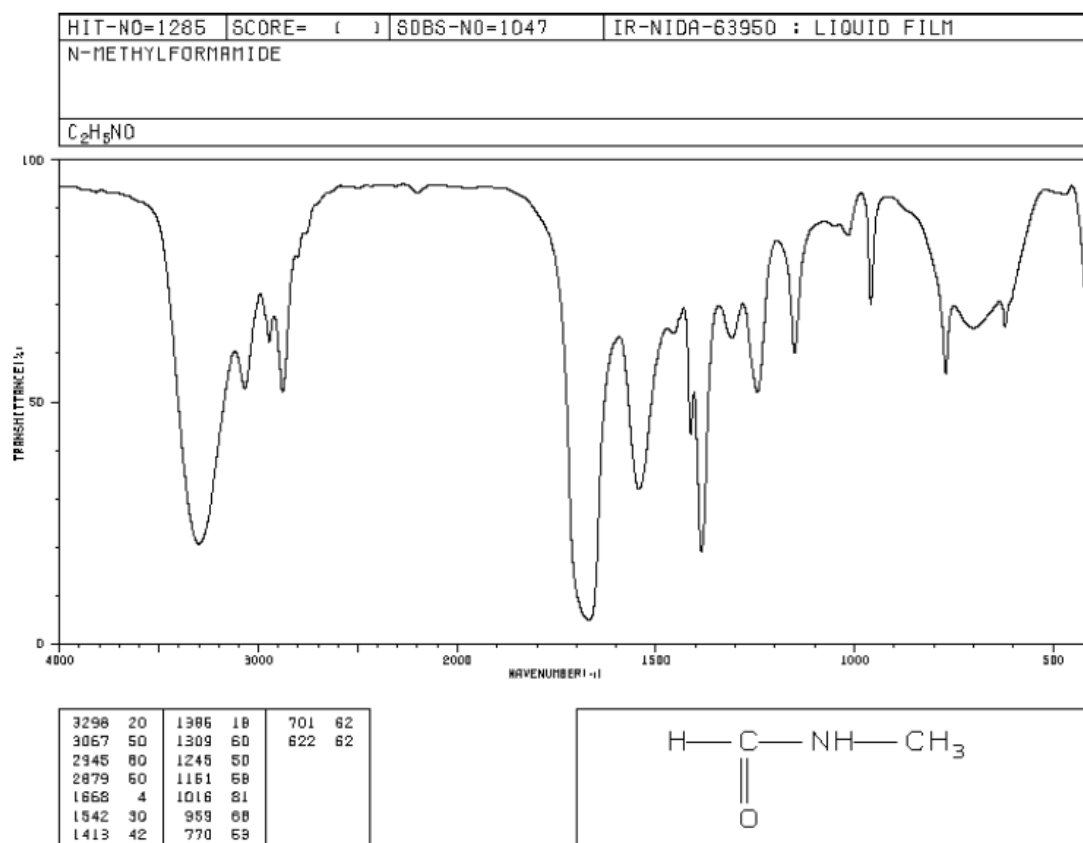
**Part II IR spectra of 1,2,4-triazole, lactic acid, *N*-methylformamide, sodium homocitrate,  $\text{K}_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{R,S-H}_2\text{homocit})_2]\cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2[\text{Mo}_3\text{SO}_3(\text{R,S-lact})_3(\text{im})_3]\cdot 10\text{H}_2\text{O}$**



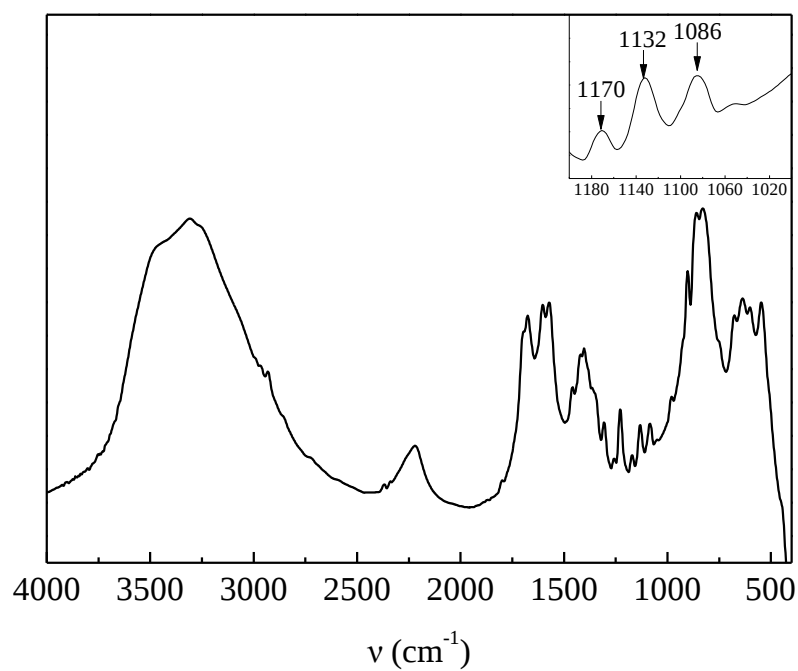
**Supplementary Fig. 23.** FT-IR spectrum of 1,2,4-triazole originated from Spectral Database for Organic Compounds SDBS. URL for this compound: <https://sdb.sdb.aist.go.jp/sdb/cgi-bin/landingpage?sdbno=3852>.



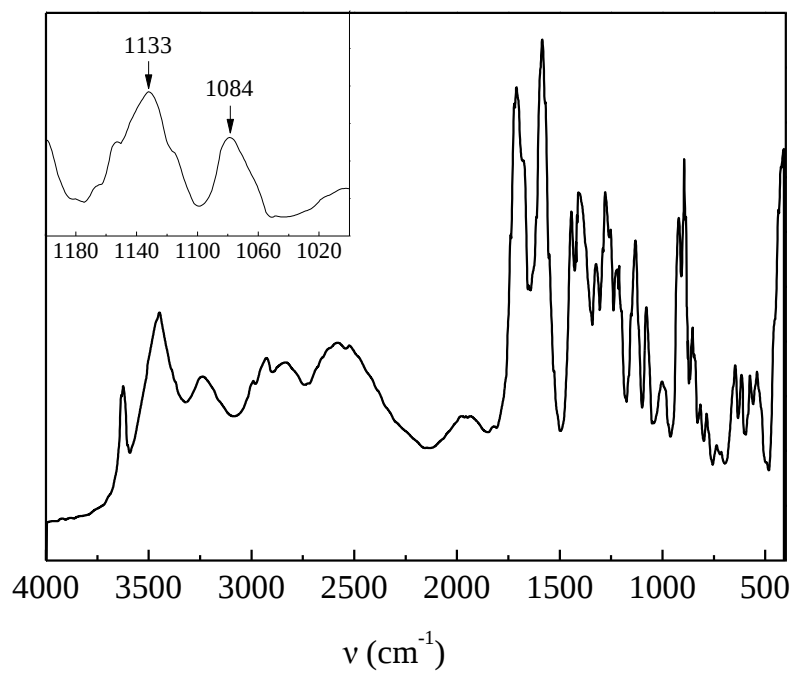
**Supplementary Fig. 24.** FT-IR spectrum of lactic acid originated from Spectral Database for Organic Compounds SDBS. The 1047  $cm^{-1}$  peak is assigned to C–OH vibration. URL for this compound: [http://sdb.db.aist.go.jp/sdb/cgi-bin/direct\\_frame\\_disp.cgi?sdbno=12682](http://sdb.db.aist.go.jp/sdb/cgi-bin/direct_frame_disp.cgi?sdbno=12682).



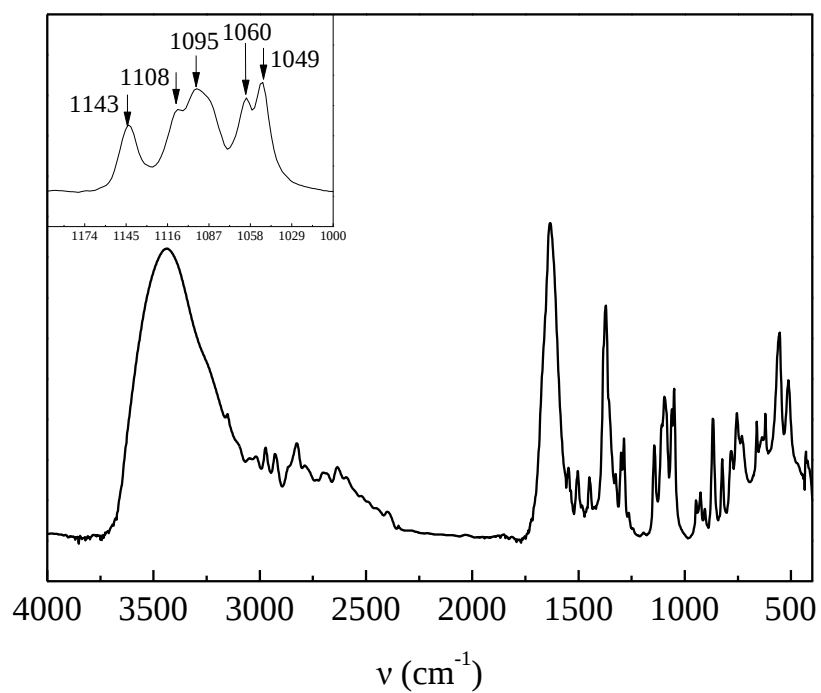
**Supplementary Fig. 25.** FT-IR spectrum of *N*-methylformamide [C<sub>2</sub>H<sub>5</sub>NO] originated from Spectral Database for Organic Compounds SDBS. URL for this compound: [https://sdb.s.db.aist.go.jp/sdb/cgi-bin/direct\\_frame\\_top.cgi](https://sdb.s.db.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi).



**Supplementary Fig. 26.** FT-IR spectrum of  $\text{Na}_3(\text{Hhomocit}) \cdot \text{H}_2\text{O} \cdot 7$ . The 1086 cm<sup>-1</sup> peak is assigned to C–O<sub>H</sub> vibration.



**Supplementary Fig. 27.** FT-IR spectrum of  $\text{K}_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{R,S-H}_2\text{homocit})_2]\cdot 2\text{H}_2\text{O}$ .<sup>7</sup> The peak at 1084  $\text{cm}^{-1}$  is assigned to C–O vibration.



**Supplementary Fig. 28.** FT-IR spectrum of  $\text{Na}_2[\text{Mo}_3\text{SO}_3(\text{R,S-lact})_3(\text{im})_3]\cdot 10\text{H}_2\text{O}$ .<sup>5</sup> The peaks at 1049, 1060 and 1056  $\text{cm}^{-1}$  are assigned to C–O vibration.

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